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A SURVEY OF VIBRATIONAL RELAXATION  
RATE DATA FOR PROCESSES IMPORTANT TO  
CO<sub>2</sub>-N<sub>2</sub>-H<sub>2</sub>O INFRARED PLUME RADIATION

Jay A. Blauer, et al

Ultrasystems, Incorporated

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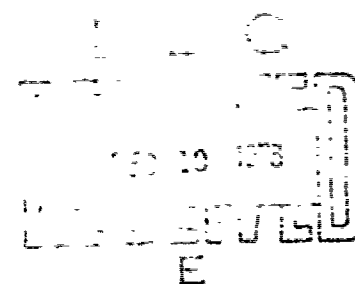
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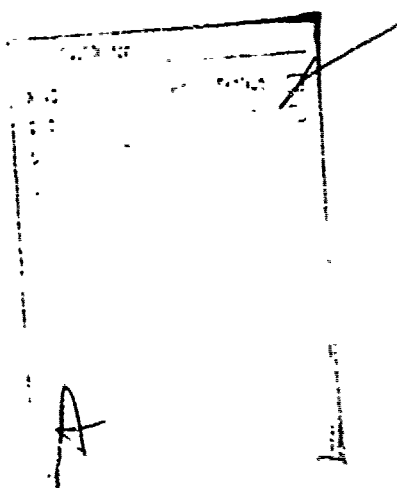
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13. ABSTRACT  A comprehensive survey of relaxation rate data important in the modeling of non-equilibrium infrared radiation from exhaust plumes at altitude is presented. A model is developed which considers energy transfer among the first fourteen vibrational states of CO <sub>2</sub> , the first five of H <sub>2</sub> O, and up to the first three states of each of the diatomic molecules considered, i.e., of N <sub>2</sub> , O <sub>2</sub> , CO, OH, and H <sub>2</sub> . Available data are first assembled for those processes that have been subjected to experimental analysis. Where possible, statistical and/or quantum considerations are used to relate unmeasured rate constants to those whose values are known. Finally, resort is made to available theory to obtain estimates for the rate constants for the balance of the interactions important to the overall model.			

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## FOREWORD

This technical report is submitted by Ultrasystems, Inc. in accordance with the provisions of Air Force Contract F04611-73-C-0032 entitled "Non-Equilibrium Radiation Model for Exhaust Plumes" and has been assigned Ultrasystems Report Number SN-8225/TR. The report was prepared for the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California.

The purpose of this report is to summarize all important V-V and T-V relaxation rate information that has been collected under Phase I of this contract. This report can be considered as a part of the final report required for the subject contract. A comprehensive literature survey of the subject matter has been conducted, and, in addition, theoretical methods have been used to estimate relaxation rates for those processes for which no experimental data could be found. The results contained in this report should prove useful to those currently modeling the chemical kinetics of either exhaust plumes or lasers that involve the molecules studied.

Work presented in this report began in November 1972 and concluded in May 1973. The program was conducted within the Engineering Sciences Department of Ultrasystems Inc. at their Irvine facility. This report was co-authored by Dr. Jay A. Blauer and Mr. Gary R. Nickerson. The Air Force Program Monitor was Lt. Peter C. Sukanek (AFRPL/DYSP).

This technical report has been reviewed and is approved.

Paul J. Daily  
Colonel, USAF  
Chief, Technology Division

# TABLE OF CONTENTS

	<u>Page No.</u>
LIST OF TABLES	v
LIST OF FIGURES	vi
1. INTRODUCTION	1
2. MECHANISM	2
3. THEORETICAL MODELS AND STATISTICAL INTER-RELATIONSHIPS	6
4. VIBRATION STATES CHOSEN FOR REVIEW AND PRELIMINARY RATE SCREENING	15
5. CURRENT STATUS OF EXPERIMENTAL RATES	16
6. SUMMARY	28
7. EXPLANATION OF THE TABLE OF RATE DATA	31
8. TABLES	33
9. FIGURES	49
REFERENCES	60

## LIST OF TABLES

	<u>Page No.</u>
I.    Vibrationally Excited Species and Energy Levels.	34
II.   Product Formation Rates for the Following Proc $\text{CO}_2(01^11) + \text{CO}_2 \rightarrow \text{CO}_2(mn^lp) + \text{CO}_2$ .	36
IIIa. V-T Intramolecular V-V Energy Transfers in $\text{CO}_2$ .	37
IIIb. Intermolecular V-V Energy Transfer Rates in $\text{CO}_2$ .	41
IIIc. Scrambling Reactions in $\text{CO}_2$ .	43
IIId. V-T and Intramolecular V-V Energy Exchanges in Species Other Than $\text{CO}_2$ .	44
IIIe. Intermolecular V-V Transfer Involving Species Other Than $\text{CO}_2$ .	46
IVa. Alternate Table of Resonant Intermolecular V-V Energy Exchange Rates Among $\text{CO}_2$ Molecules.	47
IVb. Resonant Intermolecular V-V Energy Exchange Rates Between Symmetric Stretching Modes of $\text{CO}_2$ Molecules.	47
V.    Einstein Coefficients For Spontaneous Emission.	49



## LIST OF FIGURES

	<u>Page No.</u>
1. Review of experimentally derived rate constants for the deactivation of $\text{CO}_2$ ( $01^1 0$ ) by various collision partners.	50
2. Review of experimentally derived rate constants for the deactivation of $\text{CO}_2$ ( $00^0 1$ ) by various collision partners.	51
3. Review of deactivation rates derived from theory <sup>22</sup> and experiment for the process $\text{CO}_2$ ( $00^0 1$ ) + $\text{CO}_2 \rightarrow \text{CO}_2$ ( $mn^l p$ ) + $\text{CO}_2$ .	52
4. Review of experimentally derived rate constants for the V-V energy transfers between $\text{CO}_2$ ( $00^0 1$ ) and $\text{N}_2$ (0) or CO (0).	53
5. Review of experimental data for the self deactivation of $\text{H}_2\text{O}$ ( $010$ ).	54
6. Review of experimental results for the deactivation of $\text{N}_2$ (1) by various collision partners.	55
7. Review of experimental results for the deactivation of $\text{O}_2$ (1) by $\text{O}_2$ , $\text{H}_2$ , and $\text{H}_2\text{O}$ .	56
8. Review of experimental results for the deactivation of CO (1) by various collision partners.	57
9. Review of experimental results for the V-V transfers of energy between some diatomic molecules.	58
10. Review of experimental results for the deactivation of $\text{H}_2$ (1) by $\text{H}_2$ .	59

## NOMENCLATURE

$\langle f \rangle$	molecular orientation averaging function.
$k$	bimolecular rate constant in units of cc/mole-sec.
$l$	quantum number for vibrationally induced rotational motion in $\text{CO}_2$ . also used as the range parameter of the repulsive potential function.
$m$	reduced mass of the collision pair.
$M_i$	the atomic weight of the $i^{\text{th}}$ particle of a molecule.
$M_s$	effective molecular weight for the $s^{\text{th}}$ vibrational mode.
$\bar{M}$	reduced molecular weight of the collision pair.
$P$	transition probability
$q$	the matrix element of the oscillator's internal coordinate.
$Q$	the quadrupole moment.
$s$	step number index of SSH theory
$S$	a statistical factor which accounts for the degeneracy of an energy transfer process.
$T$	absolute temperature in degrees Kelvin.
$v$	vibrational quantum number
$Z$	average number of collisions required to cause a vibrational transition.
$Z_{AB}$	bimolecular collision frequency.
$Z_{tr}$	the contribution of relative translational motion to the value of $Z$ as described in the SSH theory.
$Z_o$	a steric factor appearing in SSH theory.
$(Z_s)_{osc}$	the contribution of vibrational motion from step $s$ of an overall process to the value of $Z$ as described in the SSH theory.
$\alpha$	energy contribution of dipole-dipole attraction.
$\alpha_s^2$	a function relating Cartesian and normal vibrational coordinate.
$\beta$	energy contribution of dipole-quadrupole attraction.
$\Delta H$	enthalpy difference between an excited state and the ground state
$\Delta l$	change in the value of the quantum number, $l$ .
$\Delta v$	change in a vibrational quantum number, $v$
$\Delta 6$	vibrational energy converted to translational motion in an overall energy exchange process.

$\epsilon/k$	the Lennard-Jones attractive potential.
$\theta$	the characteristic vibrational temperature of a molecule
$\mu$	the dipole moment.
$\sigma$	Lennard-Jones collision diameter
$X_1$	transition moment.
$\Psi$	vibrational wave function.
$\omega_s$	the change in vibrational frequency during the $s^{\text{th}}$ step.

## 1. INTRODUCTION

Theoretical performance predictions of any combustion process depend not only upon assumptions regarding the species present but also upon the nature of the reactions taking place. In rocket propulsion problems, the simplifying assumption of thermodynamic equilibrium is usually made. However, for some engines performing at altitude, there is convincing experimental and analytical evidence that nonequilibrium conditions exist in both the nozzle and the freely expanding plume. Accordingly, an accurate mathematical description of plume radiation must consider the kinetic events that permit non-equilibrium conditions to exist in the flowfield.

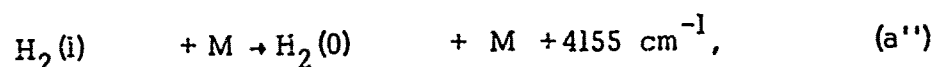
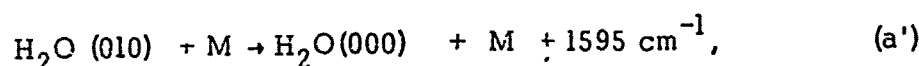
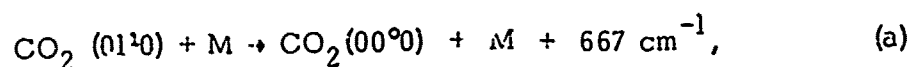
In order to obtain useful estimates of the infrared radiation from plumes at altitude, it becomes necessary to know the rates of vibrational energy transfer among the molecules that make up the plume flowfield. Although considerable information is available at the present time<sup>1-60</sup> regarding energy transfer between the major molecular species that make up typical plume environments (i.e.  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ), considerable reliance must also be made upon theoretical estimates for the rates of processes that have not been subjected to experimental investigation. Fortunately, it is frequently possible by statistical or quantum considerations to find relationships between known and unknown rate constants. In those cases for which this is not possible, recourse must be made directly to available theory.

The problem under consideration has obvious parallels to those encountered in the mathematical description of the gas dynamic laser. As such, we are able to rely heavily upon the earlier review given by Taylor and Bitterman concerning rates of importance to the  $\text{CO}_2$ - $\text{N}_2$  laser system<sup>1</sup>.

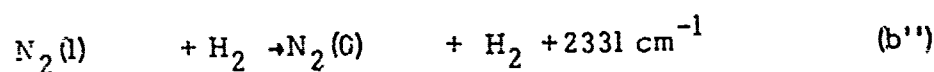
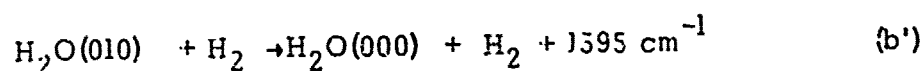
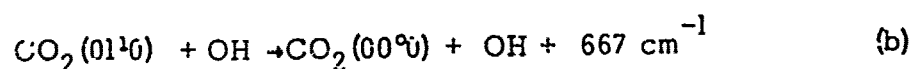
## 2. MECHANISM.

Vibrational energy transfers may be classified into at least three distinctive categories: Vibration-to-Translation (V-T), Vibration-to-Rotation-to-Translation (V-R-T), and Vibration-to-Vibration (V-V). In addition, there are two subgroupings of V-V processes depending upon whether the transfer is intermolecular or intramolecular. Examples of each of these processes are to be found in the following listing:

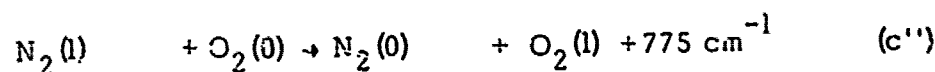
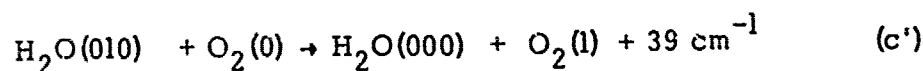
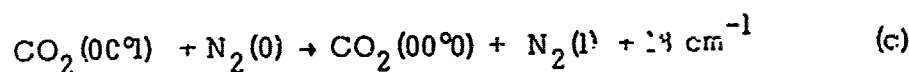
### V-T Processes



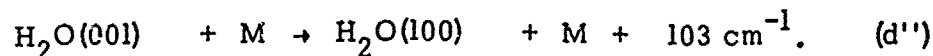
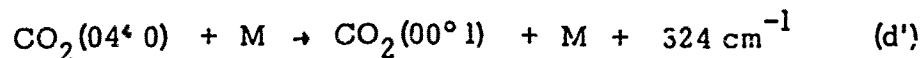
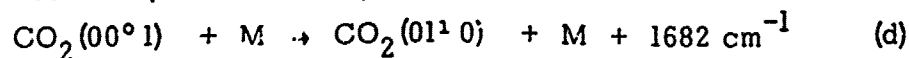
### V-R-T Processes



### V-V Processes (intermolecular)



#### V-V Processes (Intramolecular)



It has been suggested that in molecules with small moments of inertia (e.g. OH, H<sub>2</sub>O, etc.) vibrational energy may be first transferred into the rotational degrees of freedom rather than directly into translation<sup>41,56,67</sup>. Convincing evidence has been presented which suggest that in collisions with hydride like species, polyatomic molecules such as CO<sub>2</sub> and H<sub>2</sub>O are deactivated in this manner<sup>70</sup>. Accordingly, although the energy requirements for V-T and V-R-T energy transfers are the same, a distinction has been made here between these processes and they are subsequently treated by different theoretical methods.

Before proceeding further it is appropriate to briefly review nomenclature and the selection rules for vibrational transitions in CO<sub>2</sub>, H<sub>2</sub>O, and the diatomic molecules.

Carbon dioxide is a linear triatomic molecule, and as such it has three normal vibrational frequencies, one of which is degenerate. In addition, by virtue of its linear nature, it has a vibrational rotation mode about its inter-nuclear axis. Accordingly, four quantum numbers are required to completely specify its vibrational state<sup>39</sup>. A typical spectroscopic symbol for this molecule will have the form CO<sub>2</sub>(mn<sup>l</sup>p). The integers m, n, and p specify the values of the three vibrational quantum numbers  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ ; whereas, the integer  $l$  will be even or odd depending upon whether  $\nu_2$  is even or odd; furthermore, the following relationship holds:

$$l = \nu_2, \nu_2 - 2, \nu_2 - 4, \dots, 1 \text{ or } 0.$$

During a radiative transition involving the  $\text{CO}_2$  molecule, the following selection rules describe the processes which are possible<sup>46</sup>.

$$\begin{aligned}\Delta v_1 &= \pm 1, 0, \\ \Delta v_2 &= \pm 1, 0, \\ \Delta v_3 &= \pm 1, 0, \\ \Delta l &= \pm 1 \text{ whenever } \Delta v_2 = \pm 1, \\ \Delta l &= 0 \text{ whenever } \Delta v_2 = 0.\end{aligned}$$

These rules have a quantum mechanical origin and are based upon an assumption that the molecular motions involved are simple harmonic. Herzfeld and his co-workers<sup>61</sup> have treated the collision induced transfer of vibrational energy from a quantum mechanical standpoint. The basic assumption underlying their treatment is that the minimum displacement  $X$  of the oscillator nuclei from their equilibrium separation  $r_e$  during a collision is small compared to the instantaneous distance  $x$  between the incident atom and the center of mass of the oscillators. They expand the interaction energy  $U(x-X)$  as a power series in  $X$  about  $r_e$  and neglect all terms of order  $X^2$  or higher. In this approximation, for harmonic oscillators, the above simple selection rules are shown to apply. More recently, Shuler and Zwanzig<sup>42</sup> have shown that for harmonic oscillators undergoing impulsive hard sphere collisions of high energy, the simple selection rules break down and multiquantum transitions become possible. Treanor et al<sup>93</sup> have treated the problem on the basis of an anharmonic oscillator and find marked departure from the model described here under conditions of high vibrational energy coupled with low translational temperature. The net effect is to increase the rate of relaxation when the vibrational energy is high, i.e. under conditions prevailing when the energy inversion is large. Accordingly, as the temperature at which the vibrationally excited species are produced is increased we will expect increasing departure from the simple rules given above. Nevertheless, in line with the assumptions of Herzfeld and other<sup>1,15,22,61</sup> and for the sake of brevity, we will assume that the rules do apply.

Due to an accidental degeneracy between the modes  $v_1$  and  $2v_2$  in  $\text{CO}_2$  there is a mixing of the wave functions (linear combination) to form two new states that are assumed to be in local equilibrium (Fermi resonance)<sup>39</sup>. This equivalence of states is designated by placing both sets of symbols within the parenthesis. Actually, there are two states of slightly different energy that will then have the same spectroscopic symbols. They are differentiated, by primes. We have for example the states  $(02^\circ 0, 10^\circ 0)'$  and  $(02^\circ 0, 10^\circ 0)''$  at  $1285 \text{ cm}^{-1}$  and  $1388 \text{ cm}^{-1}$  above the ground state. In the present survey, only the total rate of energy flow into or out of both states is considered. Any attempt to consider all of the states in Fermi resonance individually would make the problem intractable at the present time.

The vibrational state of water requires only three quantum numbers. Accordingly, the symbol  $\text{H}_2\text{O}(mnp)$  designates that the integer values of the three quantum numbers  $v_1$ ,  $v_2$ , and  $v_3$  are  $m$ ,  $n$ , and  $p$  respectively. The selection rules that are assumed to apply for vibrational exchanges involving this molecule are as follows:

$$\begin{aligned}\Delta v_1 &= \pm 1, 0 \\ \Delta v_2 &= \pm 1, 0 \\ \Delta v_3 &= \pm 1, 0\end{aligned}$$

The vibrational state of a diatomic molecule requires only one quantum number for complete specification. Accordingly, the symbol  $\text{N}_2(n)$  specifies that there are  $n$  quanta of vibrational energy in the  $\text{N}_2$  molecule. The selection rule holding in these cases is assumed to be as follows:

$$\Delta v = \pm 1$$

Although a very large number of rates must be known for a complete specification of the vibrational energy transfer in a plume flowfield, not all routes for energy transfer are equally efficient. Accordingly, a very satisfactory description of nonequilibrium radiation can be obtained from a knowledge of a limited number of important rates. It is the intent of this compilation to not only provide rate data but also offer some guidance regarding their relative importance.



### 3. THEORETICAL MODELS AND STATISTICAL INTER-RELATIONSHIPS

Hertzfeld<sup>22</sup> has adapted the well-known SSH theory to the specific case of vibrational energy transfer in  $\text{CO}_2$  in the presence of Fermi resonance. The overall relaxation equation is written in an abbreviated form, i.e.,

$$Z = 1.017 \left( \frac{Z_0}{S} \right) Y Z_{\text{tr}} \exp \left( - \frac{\epsilon}{kT} - \frac{\Delta\theta}{2T} \right) \prod_s (Z_s)_{\text{osc}} \quad (1)$$

The quantity  $Z$  is the average number of collisions required to cause a vibrational transition to occur;  $Z_0$  is a steric factor to be discussed later;  $Z_{\text{tr}}$  is the contribution of relative translational motion to  $Z$ ; and then  $(Z_s)_{\text{osc}}$  represents the contribution of vibrational motion from steps in the overall process. These and other quantities are defined further below. It is to be noted that in multistep processes, the value for  $Z_{\text{tr}}$  is computed for the overall process, whereas, each step contributes its individual value for  $(Z_s)_{\text{osc}}$ . In equation (1)

$$Y = 0.76 \left( 1 + 1.1 \frac{\epsilon}{kT} \right)$$

$$Z_{\text{tr}} = \pi^2 \left( \frac{3}{2\pi} \right)^{1/2} \frac{(\Delta\theta)^2}{\theta'} \left( \frac{T}{\theta'} \right)^{7/6} \exp \left[ \frac{3}{2} \left( \frac{\theta'}{T} \right)^{1/2} \right]$$

The energy exchanged between vibrational and translational degrees of freedom ( $\Delta\theta$ ) refers to the overall process regardless of the number of steps.

$$\theta' = 0.8153 \tilde{M} \ell^2 (\Delta\theta)^2$$

$$(Z_s)_{\text{osc}} = 0.0413 \sigma_s^2 M_s \ell^2 \theta_s$$

One value for  $(Z_s)_{\text{osc}}$  for each step (s) in the overall process appears in the expression for  $Z$ . This  $Z$  value is strictly for a single transition, i.e., the factor  $(1 - e^{-\theta/T})$  is omitted\*.

\*In this study, the factor  $(1 - e^{-\theta/T})$  has been used only to relate deactivation rates to the experimentally observed overall deactivation rates of specific vibrational modes.

$$\theta_s = hc \omega_s / k,$$

$Z_o$  = steric factor,

$s$  = step no. index,

$S$  = a statistical factor that accounts for the degeneracy of the energy transfer process,

$\bar{M}$  = reduced molecular weight of collision pair,

$\epsilon/\lambda$  = Lennard-Jones attractive potential,

$\alpha_s$  = a function whose derivation depends upon the relationship between the cartesian vibrational coordinates of the molecule and the corresponding normal coordinates,

$\omega_s$  = the change in vibrational frequency during the  $s^{\text{th}}$  step,

$\Delta \theta$  = vibrational energy converted to transitional motion in the overall process,

$M_s$  = the effective molecular weight for the vibrational mode involved in the  $s^{\text{th}}$  step of the overall transition,

$\ell$  = the range parameter of the repulsive potential function.

The function  $\alpha_s^2$  has the following form for a  $\text{CO}_2$  molecule, the numbers 1,2,3 being applied to the atoms OCO, respectively:

$$\alpha_1^2 = \frac{1}{4},$$

$$\alpha_2^2 = \frac{4 M_1^2 + M_2^2}{2 (2 M_1 + M_2)^2},$$

$$\alpha_3^2 = \left( \frac{M_2}{2 M_1 + M_2} \right)^2.$$

Furthermore, for  $\text{CO}_2$ ,

$$M_s = M_1/2 \text{ for } s=1,$$

$$M_s = \frac{2M_1M_2}{2M_1+M_2} \text{ for } s=2,3.$$

For  $\text{H}_2\text{O}$  the function  $\alpha_s^2$  has the following form, the numbers 1,2,3 being applied to the atoms HOH, respectively:

$$\alpha_1^2 = \frac{1}{4+2M_1(\cos \theta)^2} \cdot \frac{M_2}{M_2}$$

$$\alpha_3^2 = \frac{\left(\frac{2M_1M_2}{2M_1+M_2}\right) \frac{2M_1M_2^2}{(2M_1+M_2)^2 \tan^2 \theta}}{2M_1+M_2 \left[\frac{2M_1}{M_2} \sin \theta\right]^2} \cdot$$

The value for  $\alpha_2^2$  is not needed in our argument and will not be given here. Furthermore, for  $\text{H}_2\text{O}$ ,

$$M_s = M_1/2 \text{ for } s=1,$$

$$M_s = \frac{2M_1M_2}{2M_1+M_2} \text{ for } s=2,$$

$$M_s = \frac{2M_1M_2}{2M_1+M_2} + \frac{2M_1M_2^2}{(2M_1+M_2)^2 \tan^2 \theta} \text{ for } s=3,$$

where  $\theta$  is the half angle of the isosceles triangle, formed by the two H-O bonds in the water molecule.

For a diatomic molecule,

$$\alpha_s^2 = \frac{M_1^2 + M_2^2}{2(M_1 + M_2)^2}$$

$$M_s = \frac{M_1 M_2}{M_1 + M_2}$$

The range parameter  $\ell$  was evaluated by means of method B of reference 61 and involves an iterative solution of the following two equations:

$$\frac{\epsilon_m}{k} = .5949 \left[ \tilde{M} (\omega \ell T)^2 \right]^{1/3}$$

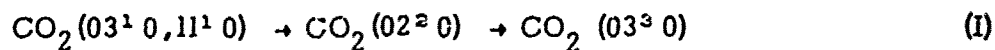
and

$$\sigma/\ell = \left\{ \ln \left( \frac{\epsilon_m}{\epsilon} + 1 \right) \left[ 1 - \left( \frac{1 + \sqrt{\frac{\epsilon_m}{\epsilon} + 1}}{2} \right) \right]^{-1/6} \right\}$$

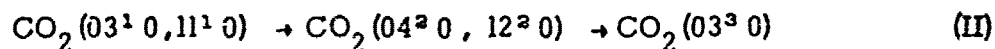
As an example of the approach followed in this review for the evaluation of the statistical factor  $\zeta$ , we consider the following transfer of energy:



Due to the selection rules, this process is treated in a two-step manner for which there are two equivalent paths of lowest energy, i.e.,



and



In accordance with the procedure outlined by Herzfeld<sup>22</sup>, we express the wave functions for the three states involved in the second path in the following manner:

$$\Psi(03^1 0, 11^1 0)' = a' \Psi_1(0) \Psi_2(3^1) + b' \Psi_1(1) \Psi_2(1^1)$$

$$\Psi(03^1 0, 11^1 0)'' = a'' \Psi_1(0) \Psi_2(3^1) + b'' \Psi_1(1) \Psi_2(1^1)$$

$$\Psi(04^2 0, 12^2 0)' = f' \Psi_1(0) \Psi_2(4^2) + g' \Psi_1(1) \Psi_2(2^2)$$

$$\Psi(04^2 0, 12^2 0)'' = f'' \Psi_1(0) \Psi_2(4^2) + g'' \Psi_1(1) \Psi_2(2^2)$$

$$\Psi(03^3 0) = \Psi_1(0) \Psi_2(3^3)$$

As before, the prime and double signatures designate states in Fermi resonance. Beginning with the singly primed states, the transition moment for this path is

$$\begin{aligned} X(\text{II}) &= \int \Psi(03^1 0, 11^1 0) \frac{z_2}{l} \Psi(04^2 0, 12^2 0) dz_1 dz_2 \\ &\quad * \int \Psi(04^2 0, 12^2 0) \frac{z_2}{l} \Psi(03^3 0) dz_1 dz_2 \\ &= \left[ a' f' \int \Psi_1(0) \Psi_1(0) dz_1 \int \Psi_2(3^1) \frac{z_2}{l} \Psi_2(4^2) dz_2 \right. \\ &\quad \left. + b' g' \int \Psi_1(1) \Psi_1(1) dz_1 \int \Psi_2(1^1) \frac{z_2}{l} \Psi_2(2^2) dz_2 \right] \\ &\quad \times f' \int \Psi_1(0) \Psi_1(0) dz_1 \int \Psi_2(4^2) \frac{z_2}{l} \Psi_2(3^3) dz_2 . \end{aligned}$$

All other terms are zero due to the orthogonal nature of the wave functions. In terms of the transition moment  $X_2$  with

$$X_2 = \int \Psi_2(1^1) \frac{z_2}{l} \Psi_2(0^0) dz_2$$

the overall transition moment for the second path becomes

$$X(\text{II}) = (a' f' \sqrt{4} + b' g' \sqrt{2}) f' \sqrt{4} X_2^2 = [4a'(f')^2 + \sqrt{8} b'(g' f')] X_2^2$$

After adding to the above the contributions which arise from the doubly primed middle term, we obtain

$$X(\text{II}) = \left[ 4a' \left[ (f')^2 + (f'')^2 \right] + \sqrt{8} b' (g'f' + g''f'')^2 \right] X_2^2$$

The orthogonality condition requires that the term in square brackets be unity; whereas, the term in parenthesis is zero. Accordingly,

$$X(\text{II}) = 4a' X_2^2$$

Since the deactivation probability and hence  $Z^{-1}$  are proportional to  $X^2$ , we have

$$X^2(\text{II}) = 16 (a')^2 X_2^4$$

Herzfeld<sup>22</sup> leaves the problem at this point to allow for considerations of states in Fermi resonance individually. Since it is our intention to treat only the total energy flux into or out of both states, we add to  $X^2(\text{II})$  the contribution due to the doubly primed initial state. Then, due to the orthogonality condition, we have for path II

$$X^2(\text{II}) = 16 X_2^4.$$

Similar considerations for path I give

$$X^2(\text{I}) = 9X_2^4$$

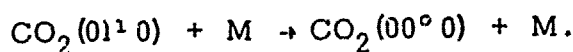
Accordingly, for the sum of both paths we obtain

$$M^2 = 25 X_2^4$$

and the statistical factor,  $S$ , for the process is 25. In accord to the treatment outlined here, the statistical factor is simply a function which accounts for the

degeneracies of the reaction paths involved in a given process. The values derived herein for S are of course only as good as the model for which they apply, i.e., that of the harmonic oscillator. Values for  $Z_0$  were obtained in the manner outlined by Herzfeld<sup>22</sup>.

The approach outlined here is very useful in obtaining statistical interrelationships between the rates of various processes. Thus, it is possible to statistically relate the rate of any process in  $\text{CO}_2$  for which  $v_2 = \pm 1$  and  $j = \pm 1$  to the experimentally determined rate of the following process:



A large number of rates treated in this review were obtained in this manner.

Although the SSH theory has proven very successful in the estimation of rates of vibrational relaxation for nonpolar molecules, for highly polar molecules of the type typified by  $\text{H}_2\text{O}$  it has been singularly unsuccessful. This is due at least in part to neglect of the attractive portion of the potential function which can be sizeable for molecules of this type. Shin<sup>37</sup> has specifically treated the case of  $\text{H}_2\text{O}$  self relaxation in a simple and entirely classical manner. His expression for the collisional transition probability with an assumption of T-V exchange is as follows:

$$P_{10} = \sqrt{\frac{4\pi}{3}} \left( \frac{4\pi m a \Delta}{\pi^2} \right) q^2 \left( \frac{\chi}{kT} \right)^{3/2} \langle f \rangle \exp \left[ -\frac{3\chi}{kT} + \frac{4\sqrt{D}\chi}{\pi kT} + \frac{16D}{3\pi^2 kT} + \frac{\Delta}{2kT} \right]. \quad (2)$$

The following definitions apply to equation (2):

$m$  = reduced mass of the collision pair,

$$a = \left[ \frac{\Gamma(7/12)}{\Gamma(1/12)} \right] \left( \frac{4D}{\chi} \right)^{1/12} \frac{\sigma}{\sqrt{\pi}},$$

$\sigma$  = the collision diameter,

$D/k = \epsilon/k$  = Lennard-Jones parameter,

$$\chi = \left[ \sqrt{m/2} \pi \Delta a k T / \hbar \right]^{2/3},$$

$\Delta$  = change in vibrational energy due to the transition,

$$\langle f \rangle = \frac{\exp(2\alpha)}{16(\alpha^2 - \beta^2)},$$

$q$  = the matrix element of the oscillator's internal coordinate,

$$\alpha = 4464 \left( \frac{\mu^2}{D \sigma^3} \right) \frac{D^{3/4} \chi^{1/4}}{k T},$$

$$\beta = 2815 \left( \frac{\mu Q}{D \sigma^4} \right) \frac{D^{2/3} \chi^{1/3}}{k T},$$

$\mu$  = the dipole moment of  $H_2O$ ,

$Q$  = the quadrupole moment of  $H_2O$ .

For the case of  $H_2O$  relaxation by a nonpolar molecule such as  $N_2$ , the value of  $\langle f \rangle$  is near unity making the calculation very simple.



Finally, Shin has also considered V-R-T exchanges in a classical manner for several specific cases<sup>56,62</sup>. For the case of the self relaxation of a hydride his equations take the form

$$P_{10} = Q' f_{vt} \sqrt{\frac{4\pi X}{kT}} \exp \left[ -\frac{3X}{kT} + \frac{8\sqrt{gDX}}{kT} + \frac{64gD}{3\pi^2 kT} + \frac{A}{2kT} \right] \quad (3)$$

Where  $Q'$ ,  $f_{vt}$ , and  $g$  are rather complicated functions of the input parameters described above, the values of which are liberally discussed in reference 55.

For this review, we have chosen to express results in terms of a kinetic rate constant  $k$  which has units of cubic centimeters per mole per second where

$$k(V-T) = \frac{1}{Z_{AB} P(V-T)}$$

and

$$k(V-V) = \frac{1}{Z_{AB} P(V-V)}$$

where  $Z_{AB}$  is the bimolecular collision frequency,  $\theta$  is the characteristic vibrational temperature of the molecule, and the expressions  $P(V-T)$  and  $P(V-V)$  refer to the collisional transitional probabilities for V-T and V-V processes respectively.

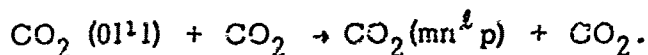
Admittedly, our expression for the rate of a V-T process depends upon an assumption of the harmonic oscillator approximation. While we recognize that, under conditions prevailing when large populations inversions are involved, departures from the model will become noticeable<sup>42,93</sup>, we have chosen to maintain the approximation in accord with other authors<sup>1,15,22,61</sup>.

Although there are other theories (e.g., those of Sharma<sup>63,64</sup>) which may be more satisfying than those of Shin from a quantum mechanical standpoint, the latter were chosen primarily for their ease of utility which apparently does not degrade their quantitative predictions to any marked degree<sup>37,56,62</sup>.

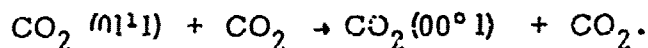
#### 4. VIBRATION STATES CHOSEN FOR REVIEW AND PRELIMINARY RATE SCREENING

This review considers the first fourteen vibrational levels of  $\text{CO}_2$ , the first five of water as well as the first two or three states of several of the more prominent diatomic species. The vibrational species considered are all tabulated in Table I along with their normal frequencies. Data for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were taken from Courtoy<sup>38</sup> and Herzberg<sup>39</sup> resp., whereas, the results for all diatomics considered were found in the JANAF Thermochemical Tables<sup>65</sup>.

In a preliminary effort to screen the deactivation rates down to a collection of tractable size, the rates of formation for all products that are created by deactivation of a given vibrational species were compared for relative magnitude at each of several temperatures up to  $3000^\circ\text{K}$ . Frequently, only one or two products were found to be favored almost to the exclusion of all others. This allowed for a ready selection of favored paths, the others being dropped from further consideration. This procedure was repeated for each of the several catalysts considered. As an example of this procedure, we present the following case:



The rates of formation for 9 different products are illustrated in Table II for a temperature of  $1500^\circ\text{K}$ . A survey of this table shows that only the following deactivation rate need be considered in this instance:



Similar results were obtained over the entire temperature range. Accordingly,  $\text{CO}_2(00^01)$  is the only product of V-T deactivation of  $\text{CO}_2(01^11)$  by  $\text{CO}_2$  that is further considered in the review. During the course of these computations, it was found that the relative amounts of the various products formed depended critically upon the temperature and only slightly upon the molecular weight of the catalyst. As a consequence, the basic conclusions drawn from Table II can be assumed to be general at  $1500^\circ\text{K}$ .

## 5. CURRENT STATUS OF EXPERIMENTAL RATES

Taylor and Bitterman (TB)<sup>1</sup> have published a very extensive review of most of the experimentally determined rates of interest to the current review. As a consequence, our first aim in this regard will be to update their review with any new data that may be available. Below, sixteen processes are discussed.



The most studied of all of the energy transfer classes considered in the present collection of rate data is that of process (i) with  $\text{M}=\text{CO}_2$ . Since the review of TB, the only significant study of this process was that published by Simpson et al<sup>15</sup>. Our selected rate is derived from a combination of these two sets of data. In a similar fashion, the rate for this process with  $\text{M}=\text{N}_2$  as derived from a combination of the results of the same two sets of authors. In this overall analysis, we have found that the ratio  $(k_{\text{N}_2}/k_{\text{CO}_2})$  changes from 0.66 at 360° K to only 0.72 at 1500° K. As a consequence, we assume that  $k_{\text{N}_2} \sim 0.7k_{\text{CO}_2}$ . Since CO and O<sub>2</sub> have molecular constants very similar to those of N<sub>2</sub>, we assume that  $k_{\text{O}_2} \sim k_{\text{N}_2} \sim k_{\text{CO}}$ .

The rate of the above process with  $\text{M}=\text{H}_2$  has also been reviewed by TB as well as in the experimental studies of Simpson and Chandler<sup>18</sup>. Although the amount of data present in this instance is far less than for the catalysts discussed above, sufficient data are available to allow for a determination of the temperature dependence of the process from 300° K up to 1100° K.

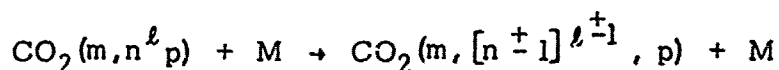
Water vapor is known to be an efficient catalyst<sup>1</sup> for the vibrational deactivation of  $\text{CO}_2(01^1 0)$ . As TB point out, there is considerable question about the actual mechanism of this process. The explanations vary from a qualitative explanation based upon the chemical affinity<sup>66</sup> between  $\text{H}_2\text{O}$  and  $\text{CO}_2$  to form  $\text{H}_2\text{CO}_3$ , to an explanation based upon an assumption of V-R exchange, made efficient by the hydride-like nature of  $\text{H}_2\text{O}$ , with an attendant small moment of

inertia<sup>56</sup>, Sharma<sup>68</sup> has estimated the magnitude and temperature dependence of this process from multipole interaction theory and an assumption of V-R energy exchange. Although this rather sophisticated calculation does reproduce the magnitude of the data, it is difficult to choose it over the results of more simple models due to the high degree of scatter in the data available. Our rate for this process is based upon a combination of the very recent results of Buchwald et al<sup>3</sup> and the results reviewed by TB. The two sets of data allow for a determination of the rate from below room temperature to above 1000°K.

Finally, the rate for M=H was considered from the standpoint of Herzfelds theoretical treatment for CO<sub>2</sub>. In order to place the value for this rate in perspective, we have made theoretical calculations also for the case of M=H<sub>2</sub>. Since the two calculations both exhibited nearly the same temperature dependence, the theory allowed for a determination of the ratio  $k_H/k_{H_2}$ .

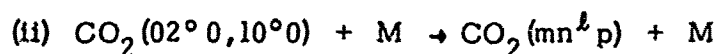
This value is reported in Table IIIa for process (i). The value for  $k_H$  is reported relative to  $k_{H_2}$  due to the fact that H<sub>2</sub> has a molecular weight near that for H and thus the theoretical expressions will have nearly the same temperature dependence making the two comparable over a wide range of conditions.

A close examination of equations (i) reveals that reactions of the type



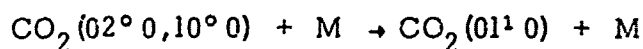
will have differences in rates due almost entirely to differences in the values of their statistical factors S. Consequently, within the approximation of the harmonic oscillator, statistical considerations alone are sufficient to relate the rates of these reactions to the experimentally derived results for process (i). A large number of rates considered in this review were evaluated in this manner.

A graphical review of experimentally derived rates for process (i) with various collision partners is illustrated in Fig. 1 and tabulated in Table III.

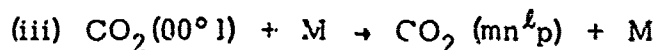


Attempts at modeling of the performance of CO<sub>2</sub> lasers usually involve an assumption that CO<sub>2</sub>(10° 0) and CO<sub>2</sub>(02° 0) are strongly coupled, i.e., they

are essentially in thermodynamic equilibrium. With this in mind, Rosser et al<sup>22</sup> have performed experiments directed toward a measurement of the deactivation rate of  $\text{CO}_2(10^0 0)$  in the presence of excess  $\text{CO}_2$  as well as in the presence of  $\text{H}_2\text{O}$ . Their method involved the injection of excess vibrationally excited species into both laser levels, following which the approach to equilibrium by radiation at both  $10.6\mu$  and  $4.3\mu$  was monitored. They reported values of  $1.87 \times 10^{10}$  cc/mole-sec and  $2.25 \times 10^{12}$  cc/mole-sec for the rates of this process at  $300^\circ\text{K}$  with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively as collision partners. Two deactivation products are possible for process (ii), i.e.,  $\text{CO}_2(01^1 0)$  and  $\text{CO}_2(00^0 0)$ . Actually,  $\text{CO}_2(02^2 0)$  can also form; however, theory<sup>22</sup> suggests that this form will be in near equilibrium with  $\text{CO}_2(02^0 0, 10^0 0)$  even at room temperature. Theory<sup>22</sup> further shows that at  $300^\circ\text{K}$  over 99% of the product will be  $\text{CO}_2(01^1 0)$ . As a consequence, we interpret these rates in terms of twice the rate of the following process:



The rate measured will be twice the rate of this process due to the degeneracy of the product. In the absence of further experimental results, resort was made to theory to obtain the dependence upon temperature for these rates. It is of interest to compare the above experimental constants with the values that can be estimated from statistical considerations and the measured rates for process (i). The statistical factor for this process is 2; accordingly, the predicted values for the rate constants at  $300^\circ\text{K}$  would be  $6.6 \times 10^9$  and  $1.7 \times 10^{13}$  cc/mole-sec for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively as collision partners. The actual value for  $\text{CO}_2$  is larger by a factor of 1.5 than the predicted rate, whereas, the experimental value for  $\text{H}_2\text{O}$  is smaller by a factor of 14. At present, it is difficult to establish the source of this discrepancy. One possible source of error is the assumption that  $\text{CO}_2(02^2 0)$  and  $\text{CO}_2(02^0 0, 10^0 0)$  are always in near equilibrium.



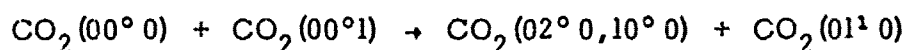
This process has lent itself readily to investigation by means of the technique of laser fluorescence in recent years<sup>1-13</sup>. In addition, shock-tube studies have been conducted at elevated temperatures, and numerous measurements based upon methods of sound dispersion have been conducted at near

room temperature<sup>1</sup>. We have added the data from recent laser fluorescence experiments<sup>3,6-13</sup> to the results reviewed by TB and by least squares analysis obtained the results plotted in Fig. 2. Due to their wide variance from the results obtained by laser fluorescence techniques, we have ignored the results of Serikov<sup>12</sup>, which were obtained by a phase method.

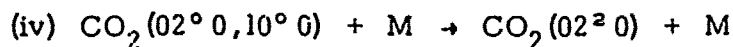
Six deactivation products are possible in the present instance:  $\text{CO}_2(03^1 0, 11^1 0)$ ,  $\text{CO}_2(03^3 0)$ ,  $\text{CO}_2(02^0 0, 10^0 0)$ ,  $\text{CO}_2(02^2 0)$ ,  $\text{CO}_2(01^1 0)$ , and  $\text{CO}_2(00^0 0)$ . The rate constant for the formation of each product was evaluated by means of the following relationship

$$k(i) = \left[ \frac{k(i)}{\sum_i k(i)} \right]_{\text{Theory}} k_{\text{expt}}$$

where  $k(i)$  is the rate constant for the formation of the  $i^{\text{th}}$  product. The term in the square brackets was evaluated with the aid of Herzfeld's development of the SSH theory for  $\text{CO}_2$ <sup>22</sup>. This analysis demonstrated that at temperatures below 3000°K only the products  $\text{CO}_2(03^1 0, 11^1 0)$ ,  $\text{CO}_2(02^0 0, 10^0 0)$  and  $\text{CO}_2(01^1 0)$  need be considered. In addition, the following process was considered in the analysis and found to be of importance:



The results of these calculations are all presented in Table IIIa.



While there are several examples of class (iv) of near resonant transfers included in Tables IIIa and IIIb, at present there are no experimental data available upon which estimates of rates can be based. As a consequence, we resort entirely to available theory. The treatment given by Herzfeld<sup>22</sup> indicates that processes of this type will always be in near equilibrium even at 300°K. Although the interpretation of the results of Rhodes et al<sup>69</sup> is open to

some questions concerning mechanism, their results seem to indicate that near resonant processes of this type are indeed rapid having rates not far removed from those given by theory<sup>1,22</sup>.



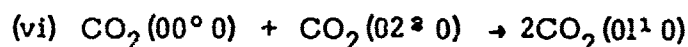
There are examples of several examples of class (v) type processes included in Table IIIa. The low rates of deactivations of this type in contrast to the rapid rates of processes of the type



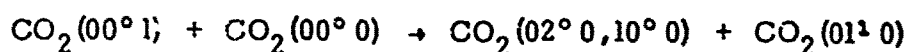
are due to the many individual steps involved in the overall case, i.e., we have in the present instance



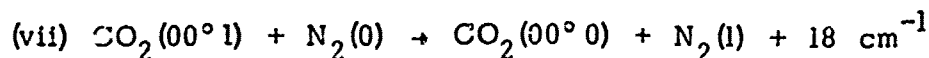
In reality, these multistep processes are slow and can be ignored except at the highest temperatures. This particular case is given merely as an example to illustrate the type of results obtained. The many steps required are the result of an application of the selection rules. No experimental data are available regarding multistep processes of this type making it necessary to rely entirely upon theory for useable estimates.



A large number of near resonant V-V transfers in  $\text{CO}_2$  are included in the present review. In the absence of any conclusive experimental results, the rates of all of these processes have been estimated by theory<sup>22</sup>. From the results of Rhodes et al<sup>69</sup> above, the rate constant at 300°K was estimated at about  $9 \times 10^{12}$  cc/mole-sec in fair agreement with the value of  $3.5 \times 10^{12}$  cc/mole-sec given by theory. Since the results of Rhodes et al<sup>69</sup> are still open to discussion concerning interpretation, we have kept the theoretical value for our review. One nonresonant V-V transfer included in our review, i.e.,



was related by theory to rates given experimentally, see (iii) above.



Of all the intermolecular V-V exchanges between unlike molecules considered in this review, this process is the nearest to energy resonance, i.e., the energy defect is only  $18 \text{ cm}^{-1}$ . Because of the near resonance, available theory<sup>22</sup> predicts a very rapid rate for the energy exchange. Indeed, it is known that this very rapid process is necessary to obtain inversion in the upper level population of the  $\text{CO}_2\text{-N}_2$  laser system<sup>1</sup>. Because of obvious parallelism between that system and the production of non-equilibrium radiation in exhaust plumes, this process can be expected to be very important in the latter case also.

Extensive experimental data are available regarding V-V transfers from  $\text{CO}_2(00^{\circ}1)$  to both  $\text{N}_2(0)$  and  $\text{CO}(0)$ <sup>8,10,14,16,17</sup>. The methods used to obtain these data involve primarily laser fluorescence<sup>8,10,14</sup> and shock tube techniques<sup>16,17</sup>. We have included all of the data from these sources in our analysis, the net result of which is illustrated in Fig. 4.



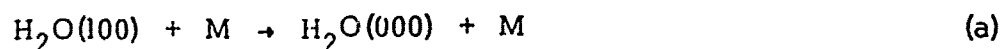
Water is known to have an extremely fast self relaxation time<sup>33-36</sup>; the probability for self deactivation per collision exceeding  $1/5$  at room temperature<sup>1</sup>. Data are available relative to this process for  $\text{M}=\text{H}_2\text{O}$  from one impact tube study<sup>33</sup> and three sound-dispersion studies<sup>34-36</sup>. The data available are somewhat scattered making it difficult to establish the temperature dependence, as shown in Fig. 5.

In an effort to estimate the temperature dependence, we have resorted to the theories of Shin<sup>37,70</sup>. Shin has developed two sets of classical equations which treat this process as a V-T exchange in one instance and a V-R-T exchange in the second case. Although the two approaches appear to give a markedly different character to the temperature dependence, they both reproduce the absolute

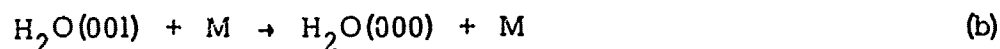


magnitude of the data reasonably well. The different types of temperature dependencies may be an illusion due to the failure to account for multipole attractive terms in the latter (V-R-T) case. Since the theoretical development of the V-T case has been more complete, and since this case does appear to reproduce the available data measureably better, we have selected the V-T method to provide information for our collection of rates.

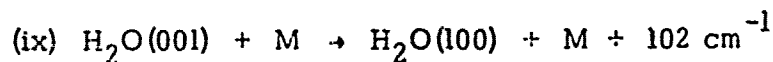
At present no data are available regarding the efficiency of other collision partners relative to this process. In the absence of required data, we have resorted to Shin's<sup>37</sup> classical V-T theory in all cases considered. This theory was also used for the following related processes:



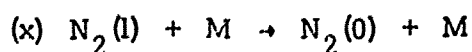
and



No experimental data are available regarding the rates of these processes making a complete resort to theory necessary; however, the success of the theory in giving rates for (viii) above leads us to accept the results with some degree of confidence.



No data are currently available regarding the rates of intramolecular V-V energy exchanges in water. In the absence of such data, we have resorted to the SSH theory<sup>61</sup>. As is to be expected for near resonant transfers of this type, the predicted rates approach collision frequency. We did not use the theories of Shin<sup>37,70</sup> here due to the fact that they have not been designed to expressly handle V-V transfers in the stepwise fashion built into the SSH theory, i.e., they do not account for seemingly important quantum effects that appear in this class of transfers.



The deactivation of  $\text{N}_2$  by itself has been extensively studied in the shock tube at elevated temperature (above  $1200^\circ\text{K}$ )<sup>71-74</sup>. In addition, data are available from sound absorption and dispersion studies<sup>75,76</sup> and one impact tube study<sup>77</sup>, all at lower temperatures (below  $1200^\circ\text{K}$ ). Unfortunately, as has been pointed out by TB only the shock-tube data appears self consistent, the rest being widely scattered. In accordance with the conclusions of TB, we assume this scatter to be due to impurities, the effects of which would be greatly magnified by the inordinately slow relaxation time at lower temperatures. Our selection of rate data are therefore taken only from the shock tube results<sup>71-74</sup>.

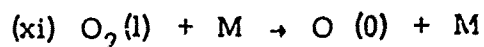
Henderson<sup>78</sup> has reported measurements based upon sound absorption which show  $\text{CO}_2$  having an efficiency nearly 3 orders of magnitude greater than that of  $\text{N}_2$  in this process. However, his interpretations of the results of his experiments are open to question<sup>1,78</sup>. As TB in their review point out, Henderson's results are surprising in that  $\text{CO}_2$  and  $\text{N}_2$  show very similar efficiencies in other processes. In the absence of further data, we have resorted to theory<sup>22</sup> to estimate the efficiency of  $\text{CO}_2$  for the purpose of this review.

Water is known to efficiently relax most diatomic molecules<sup>1</sup>. The data of Huber et al<sup>77</sup> and TB show no exception to this rule. These two studies cover a temperature range from 413 to  $1600^\circ\text{K}$  and involve impact tube as well as shock-tube techniques. Our rates for the relaxation of  $\text{N}_2(l)$  by  $\text{H}_2\text{O}$  are taken from the total collection of these two sets of data.

White<sup>79</sup> has investigated the relaxation of  $\text{N}_2(l)$  by  $\text{H}_2$  at temperatures above  $1500^\circ\text{K}$ . Although the data are limited and cover only a narrow temperature range, we have used them to estimate rates for this system. The required temperature dependence was taken from theory<sup>22</sup>.

Finally, deactivation rates for  $\text{N}_2(l)$  by  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{H}$  were evaluated directly from theory<sup>22</sup>. In the case of  $\text{H}$ , we have evaluated only the ratio  $(k_{\text{H}}/k_{\text{H}_2})$

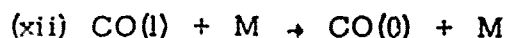
from theory and used the reported values of  $k_{H_2}$  to determine  $k_H$ . The deactivation rates for process (x) which were taken from experimental studies are all illustrated in Fig. 6.



Like process (x), the self deactivation of oxygen has been extensively studied. The data have been reviewed by TB and cover a temperature range of nearly 10,000° K. Furthermore, the experimental results were found to be in excellent agreement with theory (SSH)<sup>61</sup> over the entire temperature range. Our rate constants were taken from that compilation.

Henderson et al<sup>5</sup> have conducted sound absorption studies in  $O_2$ - $H_2O$  systems and estimate a value for the deactivation rate constant of  $O_2(l)$  by  $H_2O$  at 300° K of  $k_{H_2O} \leq 2.9 \times 10^{10}$  cc/mole-sec. We have accepted this value in the absence of further experimental data and supplied to it the temperature dependence reported for the deactivation of  $N_2(l)$  by  $H_2O$ .

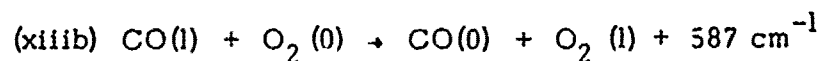
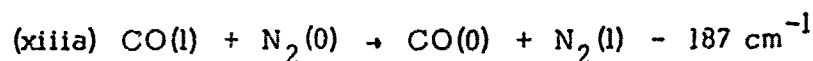
Very little data are available regarding the deactivation of  $O_2(l)$  by other collision partners. Henderson et al<sup>80</sup> claim evidence based upon sound absorption studies that  $CO_2$  is nearly 3 orders of magnitude more efficient than  $O_2$  in the relaxation of  $O_2$ ; however, their conclusions have been the subject of some argument and will not be considered further. As TB point out,  $O_2$ ,  $N_2$ , and  $CO_2$  exhibit similar efficiencies in numerous deactivation processes and it would be surprising to find either  $O_2$  or  $N_2$  to be so much less efficient than  $CO_2$  in these processes. Furthermore, neither  $N_2$  nor  $O_2$  exhibit unusual efficiencies in the deactivation of vibrationally excited  $CO_2$ . As a consequence, we rely upon the SSH theory<sup>22, 61</sup> to estimate the rate of deactivation of  $O_2(l)$  by  $CO_2$ ,  $H_2$ , and  $H$ . All deactivation rate constants which were taken from experimental results are illustrated in Fig. 7.



Since CO is infrared active with a spectral region which overlaps 4.3 $\mu$  band of  $CO_2$ , an adequate description of the radiation emitted by a plume at these wavelengths requires a knowledge of the concentrations of excited CO. This vibrational deactivation process (xii) has been extensively studied in the shock tube over a wide range of experimental conditions and in the presence of several collision partners<sup>24-28</sup>. Hooker et al<sup>27</sup> have conducted the most extensive studies of this process to date. They measured the deactivation

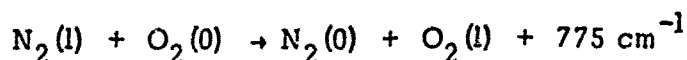
rate in the presence of  $N_2$  and  $H_2$ , as well as CO itself. The results of Matthews<sup>24</sup>, Gaydon et al<sup>25</sup>, and Windsor et al<sup>26</sup> were combined with the results of Hooker et al to give an averaged rate constant for  $M=CO$ . The results for  $M=N_2$  and  $M=H_2$  were taken directly from Hooker et al<sup>27</sup>. The rates of (12) for  $M=H_2O$  were taken directly from the shock tube results of Von Rosenberg et al<sup>40</sup>.

This system is the only one considered in this review for which data are available concerning the deactivation rate in the presence of H atoms<sup>32</sup>. The relaxation was studied under conditions of rapid nonequilibrium expansion, a shock tunnel being used to generate a nozzle flow with stagnation temperatures up to  $4500^\circ K$ . The effect of H atoms was determined by adding trace amounts of  $H_2$  to the initial gas mixture. The catalytic efficiency of H in this process is very high, the rate approaching collision frequency at temperatures above  $2000^\circ K$ . The reported steep temperature dependence for this system may be a result of the method of H atom generation; i.e., the dissociation rate of  $H_2$  itself is very temperature dependent. Furthermore, the concentration of H was not monitored. Nevertheless, the SSH theory<sup>22,61</sup> does reproduce the dependence upon temperature very well and only underestimates the rate constant by about a factor of three. Thus, at  $1500^\circ K$  theory gives a value of  $4 \times 10^{12}$  cc/mole-sec; whereas, experiment gives a value of  $1 \times 10^{13}$  cc/mole-sec. The rate constants for this system which were based upon experimental observation are illustrated in Fig. 8.



Sato et al<sup>28</sup> have applied shock tube techniques to the study of vibrational energy transfers of the above type between several pairs of diatomic molecules. In both cases, they covered a temperature range of  $1500^\circ$  to  $2500^\circ K$ . In addition to this study, Bauer et al<sup>29</sup> have studied (xiiib) at room temperature by means of a sound dispersion technique. It is of interest to note that in both of these cases, Sato et al<sup>28</sup> demonstrated that the SSH theory<sup>22,61</sup> agrees with experiment to a factor of two over the whole temperature range.

Also of interest to the present review and of the same general class as (xiii) is the following process:

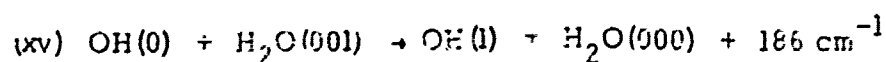


Bauer and Roesler<sup>29</sup> have estimated the rate of this process at 300°K from sound dispersion measurements on  $\text{N}_2\text{-O}_2$  mixtures. All other studies of this system were conducted with shock tubes at elevated temperatures<sup>81-83</sup>. The experimentally derived rate constants for the last three processes are illustrated in Fig. 9.



The inclusion of the hydroxyl radical into our model appears warranted due in part to its possible near resonant transfer of energy into and out of the stretching modes of the water molecule. This process has not been studied directly; however, Worley, Coltharp, and Potter<sup>84</sup> have studied the rates of deactivation of OH(9) by several diatomic and small polyatomic molecules. The rate constants ( $k \times 10^{-10} \text{ cm}^3/\text{mole-sec}$ ) of interest to the present review and which were measured were (k,M):(0.6,  $\text{O}_2$ ); (0.2,  $\text{N}_2$ ); (1.4,  $\text{CO}_2$ ); (12,  $\text{H}_2\text{O}$ ) at 300°K.

In the absence of definitive results regarding the deactivation of OH(l) by different M, we have proceeded as follows. First, the self deactivation rate ( $\text{M}=\text{OH}$ ) was estimated from the classical equations of Shin<sup>42</sup> which treat the case of the self catalyzed deactivation of a diatomic hydride (V-R-T). The harmonic oscillator approximation is then used to estimate  $k(l \rightarrow 0)$  from the measured rate  $k(9 \rightarrow 8)$  for each M of interest. The temperature dependence in each case was estimated with the aid of Shin's<sup>37</sup> equations for V-T transfer. It is interesting to note that for a temperature of 300°K, the theory estimates  $k(l \rightarrow 0)$  at  $3.6 \times 10^3 \text{ cc/mole-sec}$  for  $\text{M}=\text{N}_2$ , whereas, the harmonic oscillator approximation relative to the data of Worley et al<sup>84</sup> places the value at  $5.5 \times 10^3 \text{ cc/mole-sec}$ . The transition matrix element required by the theory for the internal vibrational coordinate of OH(l) was taken from the estimates of Potter et al<sup>85</sup> relative to their measurements of lifetimes for OH(9). In the absence of experimental data relative to CO as a collision partner, we rely entirely upon theory<sup>37</sup> for its efficiency in relationship to that of  $\text{N}_2$ , see Table IIIe.



Intermolecular energy transfer rates (V-V) between the vibrational modes of  $\text{H}_2$  and OH and the stretching modes of  $\text{H}_2\text{O}$  were estimated from the SSH theory<sup>22,61</sup>. According to theory, these exchanges are all very efficient having probabilities in the neighborhood of 0.1 or higher at 1500° K. In reality, assumptions made in the theoretical model preclude accurate predictions at these levels of efficiency; nevertheless, the order of magnitude can probably be trusted. Significantly, the equations of Shin<sup>42,62,70</sup> which treat the transfer of vibrational energy into the rotational modes (V-R-T) of hydrogen containing molecules also predict very high deactivation efficiencies. Nevertheless, we have selected rates based upon the SSH theory for these V-V transfers due to the important quantum considerations discussed under (ix) above.

The transfer of vibrational energy between  $\text{H}_2(1)$  and OH(0) was treated in a manner analogous to that described above and is reported in Table IIIe.



The vibrational relaxation of  $\text{H}_2$  has been the subject of numerous experimental investigations in recent years. Unfortunately, little is known regarding the efficiencies of collision partners other than  $\text{H}_2$  itself. The relaxation has been studied in detail at elevated temperatures in shock tubes<sup>57,86</sup>. More recently studies have been reported regarding measurements at near room temperature. These involve the use of stimulated Raman scattering<sup>58,59</sup> and somewhat indirectly, laser fluorescence<sup>87</sup>. Our self deactivation rate for  $\text{H}_2$  was derived from the sum of these experimental results which cover a temperature range from 296° K to 2700° K. The resultant rate constant is illustrated in Fig. 10 as a function of temperature.

In the absence of experimental results, the efficiencies of  $\text{N}_2$ , CO,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and H all relative to  $\text{H}_2$  were estimated from the SSH theory. The results have been entered into the table of rate data.

## 6. SUMMARY

Available rate data derived from experimental studies have been combined with results derived from current theory to provide a fairly extensive model of vibrational energy transfer for the  $\text{CO}_2\text{-N}_2\text{-CO-H}_2\text{O}$  system. Based upon the data compiled in this effort, several generalizations can be made.

As pointed out by Taylor and Bitterman<sup>1</sup>, there is a large amount of experimental data available regarding the deactivation (V-T) of  $\text{CO}_2(01^10)$  during  $\text{CO}_2\text{-CO}_2$  collisions. This state of affairs proves very fortunate due to the large number of rates that can be related statistically to the magnitude of the rate for this one process. It is disconcerting to find that contrary to available theory<sup>22</sup>,  $\text{N}_2$  and  $\text{O}_2$  appear experimentally to be slightly less efficient catalysts in this process than  $\text{CO}_2$ . At the time Taylor and Bitterman<sup>1</sup> published their review, the efficiency of  $\text{N}_2$  in this process was known primarily from highly scattered results derived from the spectrophone at or near room temperature. We have selected the more recent results of Simpson et al<sup>15</sup> which show less scatter and cover a much broader temperature range. Experimental studies regarding the efficiencies of  $\text{H}_2\text{O}$  and  $\text{H}_2$  as collision partners in process (i)\* have also recently appeared<sup>3,18</sup>. Overall, our knowledge of the parameters important in these processes is probably satisfactory.

The recent advent of the study of vibrational deactivation by the technique of laser fluorescence has proven very useful as a tool for studying the deactivation of the asymmetric stretching mode of  $\text{CO}_2$ <sup>3,8,10,11,13,14</sup>.

Indeed, the efficiencies of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{H}_2$  as collision partners in this process have all been determined by this technique. The results available from these investigations normally cover a temperature range of  $298^\circ$  up to  $1000^\circ\text{K}$ . Where possible, the temperature range has been extended for this review by inclusion of shock-tube data taken at elevated temperatures. It appears that our knowledge of the efficiencies of important collision partners relative to deactivation of the asymmetric stretching mode is quite adequate for the modeling purposes intended herein.

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\*See Section 5 for a review of process (i).

The same technique of laser fluorescence has been used to characterize the intermolecular transfer of vibrational energy between  $\text{CO}_2(00^01)$  and  $\text{N}_2(0)$  as well as  $\text{CO}(0)$ . Both of these processes seem to have been adequately studied by this technique<sup>10,14</sup>. In addition, the transfers to  $\text{N}_2(0)$  have been extensively studied in the shock-tube at elevated temperatures. Sharma and Brau<sup>64</sup> have reproduced these experimental results in a very satisfactory manner theoretically. Although their quantum theoretical model appears quite capable of reproducing experimental results for energy transfers in  $\text{CO}_2$  to at least as good an approximation as the SSH theory<sup>22</sup>, as pointed out earlier, it was judged more involved than the present review justifies.

Theory<sup>22</sup> indicates that near resonant intramolecular V-V transfers of the type



occur with very high probabilities per collision ( $P > .01$ ). At present, the only experimental evidence available regarding these processes is that of Rhodes et al<sup>69</sup> which lends support to these theoretical predictions. Nevertheless, the interpretation of these results is still open to question. If processes of this type are indeed as fast as now appears likely, modeling problems involving  $\text{CO}_2$  can be greatly simplified by assuming that states with the same value for the quantum number  $v_2$  but different quantum numbers  $l$  are in near equilibrium. This is equivalent to ignoring the quantum number  $l$  altogether. If this approach were followed, the number of vibrational transfers that would need to be considered would be greatly reduced. We offer Table IV, which contains a fairly complete set of intermolecular V-V exchanges among  $\text{CO}_2$  molecules, as an example of this approach.

At present, our knowledge of the vibrational relaxation rate for  $\text{H}_2\text{O}$  is very limited and the data are very scattered (see Fig. 5). In addition, our knowledge is limited further to the efficiency of only one collision partner,  $\text{H}_2\text{O}$  itself, and then only for the relaxation of the bending mode. Much experimental data is yet needed for this system in view of the remarkable effect  $\text{H}_2\text{O}$  has upon the vibrational lifetimes of other molecules. Work in progress at AVCO Corporation is directed toward a satisfaction of some of these needs<sup>89</sup>.



Finally, our knowledge of the effect of reactive atomic species upon the relaxation rates of important vibrational states in the system under consideration is at present limited to the single study of Von Rosenberg et al.<sup>32</sup> regarding the effect of H atoms upon the relaxation rate of CO(l) and the preliminary results of Center<sup>90</sup> concerning the effect of atomic oxygen upon the relaxation rate of CO<sub>2</sub>(01<sup>1</sup>0). Interestingly enough, in both instances it was found that these reactive atoms significantly reduce the vibrational lifetimes. Center<sup>90</sup> finds that O-atoms are about four times more efficient than CO<sub>2</sub> in relaxing CO<sub>2</sub>(01<sup>1</sup>0). Much work needs to be done in this area if the atomic species are as efficient as it now appears.<sup>94</sup>

## 7. EXPLANATION OF THE TABLE OF RATE DATA

All rate data, experimentally or theoretically derived, was expressed as a power series in temperatures,  $T^{\circ}\text{K}$ , as follows:

$$\ln k = A + BT^{-1/3} + CT^{-2/3}$$

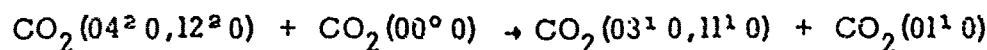
The constants A, B, and C were entered into the table. In addition, the rate constant taken directly from its source and corresponding to a temperature of  $1500^{\circ}\text{K}$  was entered.

Frequently it was possible to relate a group of rate constants to one another by means of the relative efficiencies of the collision partners involved. This treatment was possible only when the temperature dependencies of the constants involved were similar. The column headed by the symbol  $\phi$  refers to these relative efficiencies. The efficiency factor  $\phi$  is measured relative to the rate for which it is set equal to unity unless otherwise specified in the table.

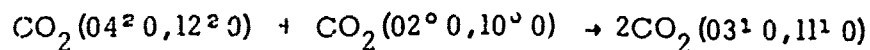
Sometimes processes occur which have two equal energy paths, but with different values of  $Z_0/S$  for each path. In this situation the rate is the sum of the rate for each path and both values of  $Z_0/S$  and shown in the Tables.

Finally, the source of each rate, theoretical or otherwise, is listed in the last column as a reference or series of references. Molecular transport properties used in this study to evaluate the theoretical rate processes by the methods presented in section 3 were taken from Hirschfelder, Curtis, and Bird<sup>91</sup>, except for the H atom properties which were taken from Svehla<sup>92</sup>.

When using the table of rate data provided herein, it is useful to keep in mind that at equilibrium the concentration of an excited molecular species relative to the concentration of the ground state falls off at higher energy levels according to the Boltzman factor ( $e^{-\Delta E/RT}$ ). As a consequence, for conditions not far removed from equilibrium the process



will be more likely to be of importance than the process



simply due to the fact that the concentration of  $\text{CO}_2(00^0 0)$  is likely to be much greater than that of  $\text{CO}_2(02^0 0, 10^0 0)$  below  $1500^\circ\text{K}$ . As the temperature increases, however, the number of individual states and thus the complexity of the mechanism must necessarily increase.

Included as Table V are the Einstein coefficients for spontaneous emission which give rise to the vibration/rotation infrared spectra of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$ .

## 8. TABLES

- I. Vibrationally Excited Species and Energy Levels.
- II. Product Formation Rates for the Following Process:  
 $\text{CO}_2 (01^11) + \text{CO}_2 \rightarrow \text{CO}_2 (mn^k p) + \text{CO}_2$ .
- IIIa. V-T Intramolecular V-V Energy Transfers in  $\text{CO}_2$ .
- IIIb. Intermolecular V-V Energy Transfer Rates in  $\text{CO}_2$ .
- IIIc. Scrambling Reactions in  $\text{CO}_2$ .
- IIId. V-T and Intramolecular V-V Energy Exchanges in Species Other Than  $\text{CO}_2$ .
- IIIe. Intermolecular V-V Transfer Involving Species Other Than  $\text{CO}_2$ .
- IVa. Alternate Table of Resonant Intermolecular V-V Energy Exchange Rates Among  $\text{CO}_2$  Molecules.
- IVb. Resonant Intermolecular V-V Energy Exchange Rates Between Symmetric Stretching Modes of  $\text{CO}_2$  Molecules.
- V. Einstein Coefficients For Spontaneous Emission.

TABLE I  
VIBRATIONALLY EXCITED SPECIES AND ENERGY LEVELS

States	$\omega(\text{cm}^{-1})$	$\omega$ (Average)	$\Delta H(\text{Kcal/mole})^*$
$\text{CO}_2(01^10)$	667.4	667.4	1.908
$\text{CO}_2(02^00, 10^00)^{'}$	1285.4	1336.8	3.821
$\text{CO}_2(02^00, 10^00)^{''}$	1388.2		
$\text{CO}_2(02^20)$	1335.2	1335.2	3.817
$\text{CO}_2(03^10, 11^10)^{'}$	1932.5	2004.7	5.730
$\text{CO}_2(03^10, 11^10)^{''}$	2076.9		
$\text{CO}_2(03^30)$	2003.3	2003.3	5.726
$\text{CO}_2(00^01)$	2349.2	2349.2	6.715
$\text{CO}_2(04^00, 12^00, 20^00)^{'}$	2548.2	2672.0	7.638
$\text{CO}_2(04^00, 12^00, 20^00)^{''}$	2670.8		
$\text{CO}_2(04^00, 12^00, 20^00)^{'''}$	2797.0		
$\text{CO}_2(04^20, 12^20)^{'}$	2584.9	2672.9	
$\text{CO}_2(04^20, 12^20)^{''}$	2760.8		
$\text{CO}_2(04^40)$	2672.8	2672.8	7.640
$\text{CO}_2(01^11)$	3004.1	3004.1	8.587
$\text{CO}_2(05^10, 13^10, 21^10)^{'}$	3181.3	3340.9	9.546
$\text{CO}_2(05^10, 13^10, 21^10)^{''}$	3339.3		
$\text{CO}_2(05^10, 13^10, 21^10)^{'''}$	3502.0		
$\text{CO}_2(05^30, 13^30)^1$	3241.5	3342.2	9.550
$\text{CO}_2(05^30, 13^30)^{12}$	3442.9		
$\text{CO}_2(05^50)$	3341.8	3341.8	9.549

$$^* \Delta H = \frac{hc}{k} \frac{R}{10^3} \omega_{\text{ave}}$$

where  $k$  = Boltzman's constant

$$\frac{hc}{k} = 1.439 \text{ cm} \cdot ^\circ\text{K}$$

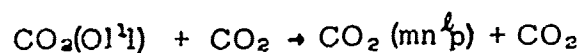
$$R = 1.987 \text{ cal} \cdot ^\circ\text{K}^{-1} \cdot \text{mole}^{-1}$$

TABLE I (Cont.)

States	$\omega(\text{cm}^{-1})$	$\Delta H(\text{Kcal/mole})$
H <sub>2</sub> O(O1O)	159 5.0	4.559
H <sub>2</sub> O(O2O)	31 51.4	9.008
H <sub>2</sub> O(10O)	3651.7	10.438
H <sub>2</sub> O(OO1)	3755.8	10.736
N <sub>2</sub> (1)	2329.5	6.659
N <sub>2</sub> (2)	4630.7	12.238
O <sub>2</sub> (1)	1556.1	4.448
O <sub>2</sub> (2)	3088.1	8.828
H <sub>2</sub> (1)	4154.7	11.876
CO(1)	2142.6	6.125
CO(2)	4258.3	12.173
OH(1)	3682.	10.526

TABLE II

Product Formation Rates\* for the Following Process:



Product	k(1500°K)	% Formed
(04 <sup>4</sup> 0)	$8.9 \times 10^4$	--
(04 <sup>2</sup> 0, 12 <sup>2</sup> 0)	$2.2 \times 10^9$	.07
(04 <sup>0</sup> 0, 12 <sup>0</sup> 0, 20 <sup>0</sup> 0)	$2.9 \times 10^9$	.09
(00 <sup>0</sup> 1)	$3.1 \times 10^{12}$	99.8
(03 <sup>1</sup> 0, 11 <sup>1</sup> 0)	$1.5 \times 10^8$	--
(03 <sup>2</sup> 0)	$7.2 \times 10^5$	--
(02 <sup>0</sup> 0, 10 <sup>0</sup> 0)	$1.5 \times 10^6$	--
(02 <sup>2</sup> 0)	$1.6 \times 10^6$	--
(01 <sup>1</sup> 0)	$2.1 \times 10^6$	--

\* Calculations based upon the theory of Herzfeld<sup>22</sup> and known rates for the deactivation of  $\text{CO}_2(01^10)$  by  $\text{CO}_2$ .

TABLE III a  
V-T AND INTRAMOLECULAR V-V ENERGY TRANSFERS IN CO<sub>2</sub>

REACTION	M	$\phi$	A	B	C	k(1500°K)	SOURCE
(01 <sup>1</sup> 0) → (00 <sup>0</sup> 0)	CO <sub>2</sub>	1.0	38.3	-177	451	2.5×10 <sup>11</sup>	1,15
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				1.8×10 <sup>11</sup>	1,15
	H <sub>2</sub>		33.0	- 83.0	345	2.2×10 <sup>13</sup>	18
	H <sub>2</sub> O		31.0	- 44.4	242	3.8×10 <sup>13</sup>	1,3
	H	0.9 <sup>‡</sup>				1.9×10 <sup>13</sup>	22
(02 <sup>0</sup> 0, 10 <sup>0</sup> 0) → (01 <sup>1</sup> 0)	CO <sub>2</sub>	1.0	39.3	-177	451	7.0×10 <sup>11</sup>	1,15,23
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				4.9×10 <sup>11</sup>	1,15,23
	H <sub>2</sub> O		29.0	- 44.4	242	5.0×10 <sup>11</sup>	1, 3,23
	H <sub>2</sub>		33.0	- 83.0	345	2.2×10 <sup>13</sup>	18,22
	H	0.9 <sup>‡</sup>				2.0×10 <sup>13</sup>	22
(02 <sup>0</sup> 0, 10 <sup>0</sup> 0) → (00 <sup>0</sup> 0)	CO <sub>2</sub>	1.0	34.1	-137		4.1×10 <sup>9</sup>	22,23
	N <sub>2</sub> , O <sub>2</sub> , CO	3.1				1.3×10 <sup>10</sup>	22
	H <sub>2</sub> O		26.8	- 44.0	242	6.2×10 <sup>10</sup>	22,23
	H <sub>2</sub>		39.5	-149	451	1.0×10 <sup>13</sup>	22
	H	1.6 <sup>‡</sup>	38.4	-131	446	1.6×10 <sup>13</sup>	22
(02 <sup>2</sup> 0) → (01 <sup>1</sup> 0)	CO <sub>2</sub>	1.0	39.0	-177	451	5.1×10 <sup>11</sup>	1,15,2
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				3.6×10 <sup>11</sup>	1,15,22
	H <sub>2</sub>		33.7	- 83.0	345	4.4×10 <sup>13</sup>	18,22
	H <sub>2</sub> O		31.7	- 44.4	242	7.6×10 <sup>13</sup>	1, 3,22
	H	0.9 <sup>‡</sup>				4.0×10 <sup>13</sup>	22
(02 <sup>0</sup> 0, 10 <sup>0</sup> 0) → (02 <sup>2</sup> 0)	CO <sub>2</sub>	1.0	36.5	- 88.9	226	1.6×10 <sup>12</sup>	27
	N <sub>2</sub> , O <sub>2</sub> , CO	0.9				1.5×10 <sup>12</sup>	22
	H <sub>2</sub>	0.13				2.1×10 <sup>13</sup>	22
	H <sub>2</sub> O	0.				5.3×10 <sup>12</sup>	22
	H	0.				1.6×10 <sup>13</sup>	22
(03 <sup>1</sup> 0, 11 <sup>1</sup> 0) → (02 <sup>2</sup> 0)	CO <sub>2</sub>	1.0	39.4	-177	451	7.6×10 <sup>11</sup>	1,15,22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				5.3×10 <sup>11</sup>	1,15,22
	H <sub>2</sub>		34.1	- 83.0	345	6.3×10 <sup>13</sup>	18,22
	H <sub>2</sub> O		32.1	- 44.4	242	1.1×10 <sup>13</sup>	1, 3,22
	H	0.9 <sup>‡</sup>				5.6×10 <sup>13</sup>	22
(03 <sup>1</sup> 0, 11 <sup>1</sup> 0) → (02 <sup>0</sup> 0, 10 <sup>0</sup> 0)	CO <sub>2</sub>	1.0	39.7	-177	451	1.0×10 <sup>12</sup>	1, 3,22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				7.0×10 <sup>11</sup>	1,15,22
	H <sub>2</sub>		34.4	- 83.0	345	8.5×10 <sup>13</sup>	18,22
	H <sub>2</sub> O		32.4	- 44.4	242	1.5×10 <sup>13</sup>	1, 3,22
	H	0.9 <sup>‡</sup>				7.7×10 <sup>13</sup>	22
(03 <sup>1</sup> 0, 11 <sup>1</sup> 0) → (01 <sup>1</sup> 0)	CO <sub>2</sub>	1.0	34.1	-137		4.1×10 <sup>9</sup>	22,23
	N <sub>2</sub> , O <sub>2</sub> , CO	3.1				1.2×10 <sup>10</sup>	22
	H <sub>2</sub>		39.5	-149	451	1.0×10 <sup>13</sup>	22
	H <sub>2</sub> O		43.0	-234	525	3.5×10 <sup>11</sup>	22
	H	1.6 <sup>‡</sup>	38.4	-131	446	1.6×10 <sup>13</sup>	22
(03 <sup>3</sup> 0) → (02 <sup>2</sup> 0)	CO <sub>2</sub>	1.0	39.4	-177	451	7.5×10 <sup>11</sup>	1,15,22
	N <sub>2</sub>	0.7				5.3×10 <sup>11</sup>	1,15,22
	H <sub>2</sub>		34.1	- 83.0	345	6.6×10 <sup>13</sup>	18,22
	H <sub>2</sub> O		32.1	- 44.4	242	1.1×10 <sup>13</sup>	1, 3,22
	H	0.9 <sup>‡</sup>				6.0×10 <sup>13</sup>	22



TABLE III a (continued)

REACTION	M	$\sigma$	A	B	C	k(1500°K)	SOURCE
(03 <sup>0</sup> 0) → (02 <sup>0</sup> 0, 10 <sup>0</sup> 0)	CO <sub>2</sub>	1.0	31.5	-171	264	1.2×10 <sup>8</sup>	22
	N <sub>2</sub>	1.8	31.1	-159	260	2.1×10 <sup>8</sup>	22
	H <sub>2</sub>		27.5	-90.1	230	1.9×10 <sup>9</sup>	22
	H <sub>2</sub> O		27.5	-90.1	230	1.9×10 <sup>9</sup>	22
	H	1.0	35.8	-244	934	1.9×10 <sup>9</sup>	22
(03 <sup>1</sup> 0, 11 <sup>1</sup> 0) → (03 <sup>0</sup> 0)	CO <sub>2</sub>	1.0	37.2	-89.3	227	3.2×10 <sup>13</sup>	22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.9				2.8×10 <sup>13</sup>	22
	H <sub>2</sub>	0.12				3.9×10 <sup>13</sup>	22
	H <sub>2</sub> O	0.33				1.1×10 <sup>13</sup>	22
	H	0.094	34.5	-84.5	213	3.0×10 <sup>13</sup>	22
(00 <sup>0</sup> 1) → (02 <sup>0</sup> 0, 10 <sup>0</sup> 0)	CO <sub>2</sub>	1.0	54.6	-404	1096	1.4×10 <sup>12</sup>	1,3, 8,13,22
	N <sub>2</sub> , CO	0.3				5.2×10 <sup>11</sup>	1,3, 8,10,22
	O <sub>2</sub>	0.4				5.6×10 <sup>11</sup>	11,22
	H <sub>2</sub>		46.5	-279	892	3.8×10 <sup>13</sup>	3,10,13,22
	H <sub>2</sub> O		27.9	+18.5	-211	1.3×10 <sup>12</sup>	6,9,10,12,22
	H	1.5 <sup>†</sup>				7.2×10 <sup>12</sup>	22
(00 <sup>0</sup> 1) → (03 <sup>1</sup> 0, 11 <sup>1</sup> 0)	CO <sub>2</sub>	1.0	43.6	-252	685	4.3×10 <sup>11</sup>	1,3, 8,13,22
	N <sub>2</sub> , CO	0.3				1.3×10 <sup>11</sup>	1,3, 8,10,22
	O <sub>2</sub>	0.4				1.7×10 <sup>11</sup>	11,22
	H <sub>2</sub>		44.2	-293	914	1.3×10 <sup>11</sup>	3,10,13,22
	H <sub>2</sub> O		19.3	+108	-397	1.5×10 <sup>11</sup>	6,9,10,12,22
	H	0.8 <sup>†</sup>				1.4×10 <sup>11</sup>	22
(00 <sup>0</sup> 1) → (00 <sup>0</sup> 0) → (02 <sup>0</sup> 0, 10 <sup>0</sup> 0) → (01 <sup>1</sup> 0)	CO <sub>2</sub>		44.0	-242	633	6.1×10 <sup>11</sup>	1,3, 8,10,22
(00 <sup>0</sup> 1) → (01 <sup>1</sup> 0)	CO <sub>2</sub>	1.0	53.9	-407	824	6.4×10 <sup>10</sup>	1,3, 8,10,22
	N <sub>2</sub> , CO	0.3				1.8×10 <sup>11</sup>	1,3, 8,10,22
	O <sub>2</sub>	0.4				2.4×10 <sup>11</sup>	11,22
	H <sub>2</sub>		47.9	-324	1053	9.6×10 <sup>11</sup>	3,10,13,22
	H <sub>2</sub> O		30.7	-54.7	-36.0	1.3×10 <sup>11</sup>	6,9,10,12,22
	H	1.9 <sup>†</sup>				1.9×10 <sup>12</sup>	22
(04 <sup>0</sup> 0, 12 <sup>0</sup> 0, 20 <sup>0</sup> 0) → (00 <sup>0</sup> 1)	CO <sub>2</sub>	1.0	30.0	-108	165	3.2×10 <sup>9</sup>	22
	N <sub>2</sub> , CO, O <sub>2</sub>	1.2	29.6	-100	161	3.8×10 <sup>9</sup>	22
	H <sub>2</sub>		28.6	-63.5	45.2	2.1×10 <sup>10</sup>	22
	H <sub>2</sub> O		29.1	-65.3	159	8.7×10 <sup>9</sup>	22
	H	0.8 <sup>†</sup>	26.3	-21.8	-101	1.6×10 <sup>10</sup>	22
(04 <sup>0</sup> 0, 12 <sup>0</sup> 0, 20 <sup>0</sup> 0) → (03 <sup>2</sup> 0)	CO <sub>2</sub>	1.0	30.2	-171	264	3.1×10 <sup>7</sup>	22
	N <sub>2</sub> , CO, O <sub>2</sub>	1.8				5.6×10 <sup>7</sup>	22
	H <sub>2</sub>		29.6	-153	520	6.5×10 <sup>8</sup>	22
	H <sub>2</sub> O						
	H	0.9 <sup>†</sup>	32.8	-197	687	5.9×10 <sup>8</sup>	22
(04 <sup>0</sup> 0, 12 <sup>0</sup> 0, 20 <sup>0</sup> 0) → (03 <sup>1</sup> 0, 11 <sup>1</sup> 0)	CO <sub>2</sub>	1.0	40.1	-177	451	1.5×10 <sup>13</sup>	1,15,22
	N <sub>2</sub> , CO, O <sub>2</sub>	0.7				1.1×10 <sup>13</sup>	1,15,22
	H <sub>2</sub>		34.8	-83.0	345	1.3×10 <sup>13</sup>	18,22
	H <sub>2</sub> O		32.8	-44.4	242	2.3×10 <sup>13</sup>	1, 3,22

TABLE III a (continued)

REACTION	M	$\phi$	A	B	C	$\kappa(1500^\circ\text{K})$	SOURCE
(34°0, 12°0, 20°0) → (02°0, 10°0)	CO <sub>2</sub>	1.0	43.7	-272	437	1.4×10 <sup>10</sup>	22
	N <sub>2</sub> , O <sub>2</sub> , CO	3.0	43.3	-254	433	4.3×10 <sup>10</sup>	22
	H <sub>2</sub>		38.8	-134	371	1.0×10 <sup>12</sup>	22
	H <sub>2</sub> O		42.2	-215	430	3.7×10 <sup>11</sup>	22
	H	1.6 <sup>†</sup>	37.7	-116	366	1.6×10 <sup>13</sup>	22
(04°0, 12°0, 20°0) → (02°0)	CO <sub>2</sub>	1.0	39.2	-271	438	1.6×10 <sup>8</sup>	22
	N <sub>2</sub> , O <sub>2</sub> , CO	3.1	38.8	-253	434	5.0×10 <sup>8</sup>	22
	H <sub>2</sub>		34.6	-133	372	1.7×10 <sup>11</sup>	22
	H <sub>2</sub> O		38.0	-214	431	6.2×10 <sup>9</sup>	22
	H	1.6 <sup>†</sup>	33.5	-114	366	2.7×10 <sup>11</sup>	22
(04°0, 12°0) → (04°0, 12°0, 20°0)	CO <sub>2</sub>	1.0	38.1	-90.4	230	7.2×10 <sup>13</sup>	22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.9	38.0	-90.8	231	6.4×10 <sup>13</sup>	22
	H <sub>2</sub>	0.12	35.6	-84.9	214	8.6×10 <sup>12</sup>	22
	H <sub>2</sub> O	0.33	36.7	-88.3	237	2.4×10 <sup>13</sup>	22
	H	0.09	35.3	-84.5	213	6.5×10 <sup>12</sup>	22
(04°0, 12°0) → (03°0)	CO <sub>2</sub>	1.0	39.7	-177	451	1.0×10 <sup>12</sup>	1, 15, 22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				7.0×10 <sup>11</sup>	1, 15, 22
	H <sub>2</sub>		34.4	-83	345	8.5×10 <sup>12</sup>	18, 22
	H <sub>2</sub> O		32.4	-44.4	242	1.5×10 <sup>13</sup>	1, 3, 22
	H	0.9 <sup>†</sup>				7.7×10 <sup>12</sup>	22
(04°0, 12°0) → (03°0, 11°0)	CO <sub>2</sub>	1.0	40.1	-177	451	1.5×10 <sup>12</sup>	1, 15, 22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				1.1×10 <sup>12</sup>	1, 15, 22
	H <sub>2</sub>		34.8	-83.0	345	1.3×10 <sup>13</sup>	13, 22
	H <sub>2</sub> O		32.8	-44.1	242	2.3×10 <sup>13</sup>	1, 3, 22
	H	0.9 <sup>†</sup>				1.2×10 <sup>13</sup>	22
(04°0, 12°0) → (04°0)	CO <sub>2</sub>	1.0	37.8	-90.4	230	5.4×10 <sup>13</sup>	22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.9	37.7	-90.8	231	4.8×10 <sup>13</sup>	22
	H <sub>2</sub>	0.12				6.5×10 <sup>12</sup>	22
	H <sub>2</sub> O	0.33				1.8×10 <sup>13</sup>	22
	H	0.09	35.0	-84.5	213	4.9×10 <sup>12</sup>	22
(04°0) → (03°0)	CO <sub>2</sub>	1.0	39.7	-177	451	1.0×10 <sup>12</sup>	1, 15, 22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				7.0×10 <sup>11</sup>	1, 15, 22
	H <sub>2</sub>		34.4	-83.0	345	8.5×10 <sup>12</sup>	18, 22
	H <sub>2</sub> O		32.4	-44.4	242	1.5×10 <sup>13</sup>	1, 3, 22
	H	0.9 <sup>†</sup>				7.7×10 <sup>12</sup>	22
(04°0) → (03°0, 01°0)	CO <sub>2</sub>	1.0	30.1	-171	264	3.0×10 <sup>7</sup>	22
	N <sub>2</sub> , O <sub>2</sub> , CO	1.6				5.2×10 <sup>7</sup>	22
	H <sub>2</sub>		29.6	-153	319	6.2×10 <sup>8</sup>	22
	H <sub>2</sub> O		29.2	-135	256	2.7×10 <sup>8</sup>	22
(01°1) → (00°1)	CO <sub>2</sub>	1.0	38.5	-177	451	3.1×10 <sup>11</sup>	1, 15, 22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				2.2×10 <sup>11</sup>	1, 15, 22
	H <sub>2</sub>		33.2	-83.0	345	2.5×10 <sup>12</sup>	18, 22
	H <sub>2</sub> O		31.1	-44.4	242	4.2×10 <sup>12</sup>	1, 3, 22
	H	0.9 <sup>†</sup>				2.3×10 <sup>12</sup>	22

TABLE III a (continued)

REACTION	M	Q	A	B	C	k(1500°K)	SOURCE
(05 <sup>1</sup> 0, 13 <sup>1</sup> 0, 21 <sup>1</sup> 0) → (05 <sup>2</sup> 0, 13 <sup>2</sup> 0)	CO <sub>2</sub>	1.0	38.4	- 88.9	226	1.1×10 <sup>14</sup>	22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.9				1.0×10 <sup>14</sup>	22
	H <sub>2</sub> O	0.33				3.7×10 <sup>13</sup>	22
	H <sub>2</sub>	0.13				1.5×10 <sup>13</sup>	22
	H	0.1				1.1×10 <sup>12</sup>	22
(05 <sup>3</sup> 0, 13 <sup>3</sup> 0) → (05 <sup>5</sup> 0)	CO <sub>2</sub>	1.0	38.4	- 88.9	226	7.5×10 <sup>13</sup>	22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.9				6.8×10 <sup>13</sup>	22
	H <sub>2</sub> O	0.33				2.5×10 <sup>13</sup>	22
	H <sub>2</sub>	0.13				9.8×10 <sup>12</sup>	22
	H	0.1				7.5×10 <sup>12</sup>	22
(05 <sup>1</sup> 0, 13 <sup>1</sup> 0, 21 <sup>1</sup> 0) → (04 <sup>2</sup> 0, 12 <sup>2</sup> 0, 20 <sup>2</sup> 0)	CO <sub>2</sub>	1.0	40.5	-177	451	2.3×10 <sup>13</sup>	1, 15, 22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				1.6×10 <sup>13</sup>	1, 15, 22
	H <sub>2</sub> O		33.2	- 44.4	242	3.4×10 <sup>13</sup>	1, 3, 22
	H <sub>2</sub>		35.2	- 83.0	345	1.9×10 <sup>13</sup>	18, 22
	H	0.9 <sup>‡</sup>				1.7×10 <sup>13</sup>	22
(05 <sup>1</sup> 0, 13 <sup>1</sup> 0, 21 <sup>1</sup> 0) → (04 <sup>2</sup> 0, 12 <sup>2</sup> 0)	CO <sub>2</sub>	1.0	40.4	-177	451	2.1×10 <sup>13</sup>	1, 15, 22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				1.5×10 <sup>13</sup>	1, 15, 22
	H <sub>2</sub> O		33.1	- 44.4	242	3.1×10 <sup>13</sup>	1, 3, 22
	H <sub>2</sub>		35.1	- 83.0	345	1.7×10 <sup>13</sup>	18, 22
	H	0.9 <sup>‡</sup>				1.5×10 <sup>13</sup>	22
(05 <sup>3</sup> 0, 13 <sup>3</sup> 0) → (04 <sup>2</sup> 0, 12 <sup>2</sup> 0)	CO <sub>2</sub>	1.0	40.4	-177	451	2.1×10 <sup>13</sup>	1, 15, 22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				1.5×10 <sup>13</sup>	1, 15, 22
	H <sub>2</sub> O		33.1	- 44.4	242	3.1×10 <sup>13</sup>	1, 3, 22
	H <sub>2</sub>		35.1	- 83.0	345	1.7×10 <sup>13</sup>	18, 22
	H	0.9 <sup>‡</sup>				1.5×10 <sup>13</sup>	22
(05 <sup>1</sup> 0, 13 <sup>3</sup> 0) → (04 <sup>4</sup> 0)	CO <sub>2</sub>	1.0	39.9	-177	451	1.3×10 <sup>13</sup>	1, 15, 22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				9.1×10 <sup>11</sup>	1, 15, 22
	H <sub>2</sub> O		32.6	- 44.4	242	1.9×10 <sup>13</sup>	1, 3, 22
	H <sub>2</sub>		34.6	- 83.0	345	1.1×10 <sup>13</sup>	18, 22
	H	0.9 <sup>‡</sup>				1.0×10 <sup>13</sup>	22
(05 <sup>5</sup> 0) → (04 <sup>4</sup> 0)	CO <sub>2</sub>	1.0	39.9	-177	451	1.3×10 <sup>13</sup>	1, 15, 22
	N <sub>2</sub> , O <sub>2</sub> , CO	0.7				9.1×10 <sup>11</sup>	1, 15, 22
	H <sub>2</sub> O		32.6	- 44.4	242	1.9×10 <sup>13</sup>	1, 3, 22
	H <sub>2</sub>		34.6	- 83.0	345	1.1×10 <sup>13</sup>	18, 22
	H	0.9				1.0×10 <sup>13</sup>	22
(05 <sup>1</sup> 0, 13 <sup>1</sup> 0, 21 <sup>1</sup> 0) → (03 <sup>1</sup> 0, 11 <sup>1</sup> 0)	CO <sub>2</sub>	1.0	35.2	-137		1.2×10 <sup>16</sup>	22
	N <sub>2</sub> , O <sub>2</sub> , CO	3.1				3.8×10 <sup>13</sup>	22
	H <sub>2</sub> O		27.9	- 44.0	242	1.7×10 <sup>11</sup>	22
	H <sub>2</sub>		40.6	-149	451	3.0×10 <sup>13</sup>	22
	H	1.6 <sup>‡</sup>				4.8×10 <sup>11</sup>	22
(05 <sup>1</sup> 0, 13 <sup>1</sup> 0) → (03 <sup>1</sup> 0)	CO <sub>2</sub>	1.0	34.1	-137		4.1×10 <sup>9</sup>	22
	N <sub>2</sub> , O <sub>2</sub> , CO	3.1				1.3×10 <sup>11</sup>	22
	H <sub>2</sub> O		26.8	- 44.0	242	6.2×10 <sup>13</sup>	22
	H <sub>2</sub>		39.5	-149	451	1.0×10 <sup>13</sup>	22
	H	1.6 <sup>‡</sup>				1.6×10 <sup>11</sup>	22

TABLE III b  
INTERMOLECULAR V-V ENERGY TRANSFER RATES IN CO<sub>2</sub>

REACTION	Z <sub>0</sub> /S	A	B	C	k(1500°K)	SOURCE
(02°0, 10°0) + (00°0) → (01°1) + (01°1)	18	34.8	-88.0	233	3.5x10 <sup>13</sup>	22
(02°0) + (00°0) → (01°1) + (01°1)	18	34.8	-88.0	233	3.5x10 <sup>13</sup>	22
(03°0, 11°0) + (00°0) → (02°0, 10°0) + (01°1)	9.9	35.7	-88.2	233	8.2x10 <sup>13</sup>	22
(03°0, 11°0) + (00°0) → (02°0) + (01°1)	12	35.2	-88.0	233	5.2x10 <sup>13</sup>	22
(03°0) + (00°0) → (02°0) + (01°1)	12	35.2	-88.0	233	5.2x10 <sup>13</sup>	22
(04°0, 12°0, 20°0) + (00°0) → (03°0, 11°0) + (01°1)	6	35.9	-88.0	233	1.0x10 <sup>13</sup>	22
(04°0, 12°0, 20°0) + (00°0) → (02°0, 10°0) + (02°0, 10°0)	3	34.9	-89.0	234	3.8x10 <sup>13</sup>	22
(04°0, 12°0) + (00°0) → (03°0, 11°0) + (01°1)	6	35.9	-88.0	233	1.0x10 <sup>13</sup>	22
(04°0, 12°0) + (00°0) → (02°0) + (02°0, 10°0)	9	33.8	-89.0	234	1.3x10 <sup>13</sup>	22
(04°0, 12°0) + (00°0) → (03°0) + (01°1)	9	35.5	-88.0	233	6.9x10 <sup>13</sup>	22
(04°0) + (00°0) → (03°0) + (01°1)	9	35.5	-88.0	233	6.9x10 <sup>13</sup>	22
(01°1) + (00°0) → (00°1) + (01°1)	36.9	34.1	-87.7	230	1.8x10 <sup>13</sup>	22
(03°0, 11°0) + (01°1) → (02°0, 10°0) + (02°0, 10°0)	4.5	36.2	-88.0	232	1.4x10 <sup>13</sup>	22
(03°0, 11°0) + (01°1) → (02°0, 10°0) + (02°0, 10°0)	6.4.5	35.7	-88.0	233	4.3x10 <sup>13</sup>	22
(03°0, 11°0) + (01°1) → (02°0) + (02°0)	6	35.9	-88.0	233	1.0x10 <sup>13</sup>	22
(03°0) + (01°1) → (02°0) + (02°0)	6	35.9	-88.0	233	1.0x10 <sup>13</sup>	22
(03°0) + (01°1) → (02°0) + (02°0, 10°0)	6	35.9	-88.0	233	1.0x10 <sup>13</sup>	22
(04°0, 12°0, 20°0) + (01°1) → (03°0, 11°0) + (02°0)	3	36.6	-88.0	233	2.0x10 <sup>13</sup>	22
(04°0, 12°0, 20°0) + (01°1) → (03°0, 11°0) + (02°0, 10°0)	3.3	36.7	-88.2	233	2.3x10 <sup>13</sup>	22
(04°0, 12°0) + (01°1) → (03°0, 11°0) + (02°0)	3.9	36.6	-88.0	233	2.1x10 <sup>13</sup>	22
(04°0, 12°0) + (01°1) → (03°0, 11°0) + (02°0, 10°0)	3	36.6	-88.0	233	2.0x10 <sup>13</sup>	22
(04°0) + (01°1) → (03°0) + (02°0)	4.5	36.2	-88.0	233	1.4x10 <sup>13</sup>	22
(04°0) + (01°1) → (03°0) + (02°0, 10°0)	4.5	36.2	-88.0	233	1.4x10 <sup>13</sup>	22
(01°1) + (01°1) → (00°1) + (02°0)	18	34.8	-88.0	233	3.5x10 <sup>13</sup>	22
(01°1) + (01°1) → (00°1) + (02°0, 10°0)	18	34.8	-88.0	233	3.5x10 <sup>13</sup>	22
(04°0, 12°0, 20°0) + (02°0, 10°0) → 2(03°0, 11°0)	1.5	37.3	-88.0	233	4.0x10 <sup>13</sup>	22
(04°0, 12°0) + (02°0, 10°0) → 2(03°0, 11°0)	1.5	37.3	-88.0	233	4.0x10 <sup>13</sup>	22
(04°0, 12°0) + (02°0, 10°0) → (03°0) + (03°0, 11°0)	2.25	36.9	-88.0	233	2.8x10 <sup>13</sup>	22
(04°0, 12°0) + (02°0, 10°0) → (02°0) + (04°0, 12°0, 20°0)	3.0	34.9	-89.0	234	3.8x10 <sup>13</sup>	22
(04°0) + (02°0, 10°0) → (03°0) + (03°0, 11°0)	2.25	36.9	-88.0	234	2.8x10 <sup>13</sup>	22
(01°1) + (02°0, 10°0) → (00°1) + (03°0, 11°0)	9	35.5	-88.0	233	6.9x10 <sup>13</sup>	22
(04°0, 12°0, 20°0) + (02°0) → (03°0, 11°0) + (03°0)	2	37.0	-88.0	233	3.0x10 <sup>13</sup>	22
(04°0, 12°0, 20°0) + (02°0) → (03°0, 11°0) + (03°0, 11°0)	2	37.0	-88.0	233	3.0x10 <sup>13</sup>	22
(04°0, 12°0) + (02°0) → (03°0, 11°0) + (03°0, 11°0)	2	37.0	-88.0	233	3.0x10 <sup>13</sup>	22
(04°0, 12°0) + (02°0) → (03°0, 11°0) + (03°0)	2.3	37.5	-88.0	233	5.0x10 <sup>13</sup>	22
(04°0, 12°0) + (02°0) → (03°0) + (03°0)	3	36.6	-88.0	233	2.0x10 <sup>13</sup>	22
(04°0) + (02°0) → (03°0) + (03°0)	3	36.6	-88.0	233	2.0x10 <sup>13</sup>	22
(04°0) + (02°0) → (03°0) + (03°0, 11°0)	3	36.6	-88.0	233	2.0x10 <sup>13</sup>	22
(01°1) + (02°0) → (00°1) + (03°0)	12	35.2	-88.0	233	5.2x10 <sup>13</sup>	22
(01°1) + (02°0) → (00°1) + (03°0, 11°0)	12	35.2	-88.0	233	5.2x10 <sup>13</sup>	22
(01°1) + (03°0, 11°0) → (00°1) + (04°0, 12°0, 20°0)	6	35.9	-88.0	233	1.0x10 <sup>13</sup>	22
(01°1) + (03°0, 11°0) → (00°1) + (04°0, 12°0)	6	35.9	-88.0	233	1.0x10 <sup>13</sup>	22
(01°1) + (03°0) → (00°1) + (02°0)	12	35.2	-88.0	233	5.2x10 <sup>13</sup>	22

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TABLE III b (continued)

REACTION	Z <sub>0</sub> /S	A	B	C	$\lambda(1500^\circ\text{K})$	SOURCE
$(05^0, 13^1, 21^1) + (00^0) \rightarrow (04^0, 12^0, 20^0) + (01^1)$	4	36.3	- 88.0	232	$1.5 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (00^0) \rightarrow (04^0, 12^0) + (01^1)$	4.5	36.2	- 88.0	233	$1.4 \times 10^{14}$	22
$(05^0, 13^1, 21^1) + (01^1) \rightarrow (04^0, 12^0, 20^0) + (02^0)$	2.0	37.6	- 88.0	233	$3.0 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (01^1) \rightarrow (04^0, 12^0, 20^0) + (02^0, 10^0)$	2.0	37.5	- 88.0	233	$3.0 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (01^1) \rightarrow (04^0, 12^0) + (01^1)$	2.25	36.9	- 88.0	233	$2.6 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (01^1) \rightarrow (04^0, 12^0) + (02^0, 10^0)$	2.25	36.9	- 88.0	233	$2.6 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (02^0) \rightarrow (04^0, 12^0, 20^0) + (03^0)$	1.33	37.4	- 88.0	233	$4.7 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (02^0) \rightarrow (04^0, 12^0, 20^0) + (03^0, 11^1)$	1.33	37.4	- 88.0	233	$4.7 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (02^0) \rightarrow (04^0, 12^0) + (03^0)$	1.5	37.3	- 88.0	233	$4.3 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (02^0) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	1.5, 3	37.5	- 88.0	233	$5.2 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (02^0, 10^0) \rightarrow (04^0, 12^0, 20^0) + (03^0, 11^1)$	1.3	37.8	- 88.0	233	$7.1 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (02^0, 10^0) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	1.13	37.6	- 88.0	233	$5.7 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow 2(04^0, 12^0, 20^0)$	0.67	38.1	- 88.0	233	$9.6 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (03^0, 11^1) \rightarrow (04^0, 12^0, 20^0) + (04^0, 12^0)$	0.67	38.1	- 88.0	233	$9.6 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (03^0) \rightarrow (04^0, 12^0, 20^0) + (04^0)$	1.0	37.7	- 88.0	233	$6.4 \times 10^{13}$	22
$(05^0, 13^1, 21^1) + (03^0) \rightarrow 2(04^0, 12^0)$	1.13	37.6	- 88.0	233	$5.7 \times 10^{13}$	22
$(05^0, 13^1) + (00^0) \rightarrow (04^0, 12^0) + (01^1)$	4.5	36.2	- 88.0	233	$1.4 \times 10^{13}$	22
$(05^0, 13^1) + (00^0) \rightarrow (04^0) + (01^1)$	7.2	35.7	- 88.0	233	$3.7 \times 10^{13}$	22
$(05^0, 13^1) + (01^1) \rightarrow (04^0, 12^0) + (02^0, 10^0)$	2.25	36.9	- 88.0	233	$2.6 \times 10^{13}$	22
$(05^0, 13^1) + (01^1) \rightarrow (04^0) + (02^0, 10^0)$	3.6	36.4	- 88.0	233	$1.7 \times 10^{13}$	22
$(05^0, 13^1) + (01^1) \rightarrow (04^0, 12^0) + (02^0)$	2.25	36.9	- 88.0	233	$2.8 \times 10^{13}$	22
$(05^0, 13^1) + (01^1) \rightarrow (04^0) + (02^0)$	3.6	36.4	- 88.0	233	$1.7 \times 10^{13}$	22
$(05^0, 13^1) + (02^0, 10^0) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	1.13	37.6	- 88.0	233	$5.7 \times 10^{13}$	22
$(05^0, 13^1) + (02^0, 10^0) \rightarrow (04^0) + (03^0, 11^1)$	3.6	36.4	- 88.0	233	$1.7 \times 10^{13}$	22
$(05^0, 13^1) + (02^0) \rightarrow (04^0, 12^0) + (03^0, 11^1)$	1.5	37.3	- 88.0	233	$4.3 \times 10^{13}$	22
$(05^0, 13^1) + (02^0) \rightarrow (04^0, 12^0) + (03^0)$	1.5, 3	37.5	- 88.0	233	$5.3 \times 10^{13}$	22
$(05^0, 13^1) + (02^0) \rightarrow (04^0) + (03^0, 11^1)$	2.4	36.8	- 88.0	233	$2.6 \times 10^{13}$	22
$(05^0, 13^1) + (02^0) \rightarrow (04^0) + (03^0)$	2.4	36.8	- 88.0	233	$2.6 \times 10^{13}$	22
$(05^0) + (00^0) \rightarrow (04^0) + (01^1)$	7.2	35.7	- 88.0	233	$8.7 \times 10^{13}$	22
$(05^0) + (01^1) \rightarrow (04^0) + (02^0)$	3.6	36.4	- 88.0	233	$1.7 \times 10^{13}$	22
$(05^0) + (01^1) \rightarrow (04^0) + (02^0, 10^0)$	3.6	36.4	- 88.0	233	$1.7 \times 10^{13}$	22
$(05^0) + (02^0) \rightarrow (04^0) + (03^0, 11^1)$	2.4	36.3	- 88.0	233	$2.6 \times 10^{13}$	22
$(05^0) + (02^0) \rightarrow (04^0) + (03^0)$	2.4	36.3	- 88.0	233	$2.6 \times 10^{13}$	22
$(05^0) + (02^0, 10^0) \rightarrow (04^0) + (03^0, 11^1)$	1.8	37.1	- 88.0	233	$3.4 \times 10^{13}$	22

TABLE III c  
SCRAMBLING ‡ REACTIONS IN CO<sub>2</sub>

REACTION	Z <sub>0</sub>	A	B	C	k (1500°K)	SOURCE
(02°0, 10°0) + (01°0) → (01°0) + (02°0)	9	35.5	-88.0	233	6.9 × 10 <sup>12</sup>	22
(03°0, 11°0) + (02°0, 10°0) → (02°0) + (03°0, 11°0)	4	36.3	-88.0	233	1.5 × 10 <sup>13</sup>	22
(03°0, 11°0) + (02°0) → (02°0) + (03°0)	4	36.3	-88.0	233	1.5 × 10 <sup>13</sup>	22
(03°0, 11°0) + (02°0) → (02°0, 10°0) + (03°0)	3	36.6	-88.0	233	2.0 × 10 <sup>13</sup>	22
(03°0, 11°0) + (02°0) → (02°0, 10°0) + (03°0, 11°0)	3	36.6	-88.0	233	2.0 × 10 <sup>13</sup>	22
(04°0, 12°0, 20°0) + (03°0, 11°0) → (03°0, 11°0) + (04°0, 12°0)	1	37.7	-88.0	233	6.0 × 10 <sup>13</sup>	22
(04°0, 12°0) + (03°0, 11°0) → (03°0) + (04°0, 12°0)	1.5	37.3	-88.0	233	4.0 × 10 <sup>13</sup>	22
(04°0, 12°0) + (03°0, 11°0) → (03°0) + (04°0, 12°0, 10°0)	1.5	37.3	-88.0	233	4.0 × 10 <sup>13</sup>	22
(04°0, 12°0, 20°0) + (03°0) → (03°0, 11°0) + (04°0)	1.5	37.3	-88.0	233	4.0 × 10 <sup>13</sup>	22
(04°0, 12°0) + (03°0) → (03°0, 11°0) + (04°0)	1.5	37.3	-88.0	233	4.0 × 10 <sup>13</sup>	22
(04°0, 12°0) + (03°0) → (03°0) + (04°0)	2.25	36.9	-88.0	233	2.8 × 10 <sup>13</sup>	22
(04°0, 12°0) + (03°0) → (03°0, 11°0) + (04°0, 12°0)	1.5	37.3	-88.0	233	4.0 × 10 <sup>13</sup>	22

‡ Reactions involving changes only in the quantum no.  $\ell$ .

TABLE III d  
V-T AND INTRAMOLECULAR V-V ENERGY EXCHANGES IN SPECIES OTHER THAN CO<sub>2</sub>

REACTION	M	$\sigma$	A	B	C	$k(1500^\circ K)$	SOURCE
$H_2O(010) \rightarrow H_2O(000)$	H <sub>2</sub> O	1.0	52.8	-363	1462	$1.0 \times 10^{14}$	33-37
	N <sub>2</sub> , O <sub>2</sub> , CO		48.5	-243	573	$4.3 \times 10^{13}$	37
	CO <sub>2</sub>		50.8	-300	813	$2.3 \times 10^{13}$	37
	H <sub>2</sub>		35.2	-14.0		$6.0 \times 10^{14}$	37*
	H	1.4 $\frac{1}{2}$				$8.4 \times 10^{14}$	37*
$H_2O(020) \rightarrow H_2O(010)$	H <sub>2</sub> O		53.5	-363	1452	$2.0 \times 10^{14}$	33-37
	N <sub>2</sub> , O <sub>2</sub> , CO		49.2	-243	558	$9.8 \times 10^{13}$	37
	CO <sub>2</sub>		51.5	-300	813	$4.6 \times 10^{13}$	37
	H <sub>2</sub>		35.2	-14.0		$6.0 \times 10^{14}$	37*
	H	1.4 $\frac{1}{2}$				$8.4 \times 10^{14}$	37*
$H_2O(001) \rightarrow H_2O(000)$	H <sub>2</sub> O	1.0	55.1	-522	1599	$5.5 \times 10^{14}$	37
	N <sub>2</sub> , O <sub>2</sub> , CO		53.9	-451	1131	$1.2 \times 10^{15}$	37
	CO <sub>2</sub>		55.8	-512	1354	$2.1 \times 10^9$	37
	H <sub>2</sub>		46.5	-273	1059	$2.3 \times 10^{13}$	37
	H		44.7	-224	939	$1.0 \times 10^{14}$	37
$H_2O(100) \rightarrow H_2O(000)$	H <sub>2</sub> C	1.0	58.6	-541	2084	$6.4 \times 10^{11}$	37
	N <sub>2</sub> , O <sub>2</sub> , CO		55.3	-435	1079	$1.3 \times 10^{11}$	37
	CO <sub>2</sub>		57.7	-503	1331	$2.4 \times 10^{10}$	37
	H <sub>2</sub> O		58.6	-541	2084	$6.4 \times 10^{11}$	37
	H <sub>2</sub>		47.2	-229	321	$3.4 \times 10^{14}$	37
	H		46.6	-218	920	$5.4 \times 10^{14}$	37
$H_2O(001) + H_2O(100)$	H <sub>2</sub> O	1.0	36.9	-88.7	250	$3.1 \times 10^{13}$	22*
	N <sub>2</sub>	1.4				$4.3 \times 10^{13}$	22
	H <sub>2</sub>	0.6				$1.9 \times 10^{13}$	22
	CO <sub>2</sub>	1.7				$5.3 \times 10^{17}$	22
	H	0.5				$1.5 \times 10^{13}$	22
$N_2(1) \rightarrow N_2(0)$	H	2.1 $\frac{1}{2}$				$1.8 \times 10^{11}$	22
	N <sub>2</sub> , O <sub>2</sub> , CO	1.0	42.2	-292		$1.8 \times 10^7$	1, 22
	CO <sub>2</sub>	0.14				$2.5 \times 10^6$	1, 22
	H <sub>2</sub> O		38.3	-124		$2.5 \times 10^{11}$	1
	H <sub>2</sub>		32.7	-90.2		$6.0 \times 10^{10}$	1, 4
$N_2(1) + N_2(1)$	N <sub>2</sub> , O <sub>2</sub> , CO	1.0	42.9	-292		$3.6 \times 10^7$	1, 22
	CO <sub>2</sub>	0.14				$5.0 \times 10^6$	1, 22
	H <sub>2</sub> O		39.0	-124		$1.7 \times 10^{13}$	1, 22
	H <sub>2</sub>		33.4	-90.2		$1.2 \times 10^{11}$	1, 4, 22
	H $\frac{1}{2}$	3.1				$3.6 \times 10^{11}$	22
$O_2(1) \rightarrow O_2(0)$	N <sub>2</sub> , O <sub>2</sub> , CO	1.0	36.6	-158		$7.9 \times 10^9$	1, 22
	CO <sub>2</sub>	0.3				$2.4 \times 10^9$	1, 22
	H <sub>2</sub> O		42.6	-124		$6.2 \times 10^{13}$	1, 43
	H <sub>2</sub>		33.0	-56.6		$6.4 \times 10^{11}$	88
	H	1.7				$1.1 \times 10^{13}$	22

TABLE III d (continued)  
V-T AND INTRAMOLECULAR V-V ENERGY EXCHANGES IN SPECIES OTHER THAN CO<sub>2</sub>

REACTION	M	Q	A	B	C	k(1500°K)	SOURCE
O <sub>2</sub> (2) + O <sub>2</sub> (1)	N <sub>2</sub> , C <sub>2</sub> , CO	1.0	37.3	-158		1.6×10 <sup>10</sup>	1,22
	CO <sub>2</sub>	0.3				4.8×10 <sup>9</sup>	1,22
	H <sub>2</sub> O		43.3	-124		1.3×10 <sup>14</sup>	1,22
	H <sub>2</sub>		33.7	-66.6		1.3×10 <sup>12</sup>	83,22
	H	1.7				2.2×10 <sup>17</sup>	22
CO(1) + CO(0)	CO	1.0	41.2	-244		4.3×10 <sup>8</sup>	24-27
	N <sub>2</sub> , O <sub>2</sub>		42.1	-289		3.1×10 <sup>7</sup>	27,22
	H <sub>2</sub>		37.9	-176	383	1.1×10 <sup>11</sup>	27
	H <sub>2</sub> O		24.3	+146	-1246	9.5×10 <sup>11</sup>	40
	H		44.4	-164		1.1×10 <sup>13</sup>	32
CO(2) + CO(1)	CO	1.0	41.9	-244		8.7×10 <sup>8</sup>	24-27,22
	N <sub>2</sub> , O <sub>2</sub>		43.2	-289		6.3×10 <sup>7</sup>	27,22
	H <sub>2</sub>		38.6	-176	383	2.2×10 <sup>11</sup>	27,22
	H <sub>2</sub> O		25.0	+146	-1246	1.9×10 <sup>13</sup>	40,22
	H		45.1	-164		2.3×10 <sup>13</sup>	32,22
OH(1) + OH(0)	OH		42.0	-243	762	3.5×10 <sup>11</sup>	56
	N <sub>2</sub>	1.0	39.3	-210		1.3×10 <sup>9</sup>	37
	O <sub>2</sub>	3.0					37
	CO	1.0					
	CO <sub>2</sub>	7.0					
	H <sub>2</sub> O	60					
H <sub>2</sub> (1) + H <sub>2</sub> (0)	H <sub>2</sub>	1.0	40.4	-227	529	5.2×10 <sup>11</sup>	57,58,59
	N <sub>2</sub> , O <sub>2</sub> , CO	0.08				4.2×10 <sup>11</sup>	22
	CO <sub>2</sub>	0.07				3.6×10 <sup>10</sup>	22
	H	2.2				1.1×10 <sup>12</sup>	22
	H <sub>2</sub> O	0.23				1.2×10 <sup>11</sup>	22



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$\text{CO}(1)+\text{N}_2(0) \rightarrow \text{CO}(0)+\text{N}_2(1)$	9	32.6				
$\text{CO}_2(00^01)+\text{CO}(0) \rightarrow \text{CO}_2(00^00)+\text{CO}(1)$	9	28.7	0.0	- 153	$4.5 \times 10^{11}$	14
$\text{CO}_2(01^11)+\text{CO}(0) \rightarrow \text{CO}_2(01^10)+\text{CO}(1)$	9	28.7	0.0	- 153	$4.5 \times 10^{11}$	14, 22
$\text{H}_2(1)+\text{H}_2\text{O}(000) \rightarrow \text{H}_2(0)+\text{H}_2\text{O}(001)$	9	35.6	- 67.0	62.1	$1.4 \times 10^{13}$	22
$\text{H}_2(1)+\text{H}_2\text{O}(000) \rightarrow \text{H}_2(0)+\text{H}_2\text{O}(100)$	9	39.1	-138	390	$1.7 \times 10^{13}$	22
$\text{H}_2(1)+\text{OH}(0) \rightarrow \text{H}_2(0)+\text{OH}(1)$	9	43.1	-232	839	$3.2 \times 10^{12}$	22
$\text{H}_2\text{O}(001)+\text{OH}(0) \rightarrow \text{H}_2\text{O}(000)+\text{OH}(1)$	9	36.5	- 62.5	16.9	$3.4 \times 10^{13}$	22
$\text{H}_2\text{O}(100)+\text{OH}(0) \rightarrow \text{H}_2\text{O}(000)+\text{OH}(1)$	9	36.6	- 62.5	17.0	$3.7 \times 10^{13}$	22

Notations:

† Measured Relative to  $k_{\text{H}_2}$ .

• Collision Frequency

•• Molecular wt. of collision partner ( $\text{H}_2\text{O}$ ) set to  $1/\sigma^2 = 3.96$  in equation<sup>-1</sup> for  $P_{10}$  to account for R-V interaction. Energy exchanged by single quantum steps.

TABLE IVa.

ALTERNATE TABLE OF RESONANT INTERMOLECULAR V-V  
ENERGY EXCHANGE RATES AMONG CO<sub>2</sub> MOLECULES

REACTION	Z <sub>0</sub> /S	A	B	C	k(1500°K)	SOURCE
(m2p) + (000) → (m1p) + (010)	18	34.8	-88.0	233	3.5×10 <sup>13</sup>	22
(m3p) + (000) → (m2p) + (010)	12	35.2	-88.0	233	5.2×10 <sup>13</sup>	22
(m4p) + (000) → (m3p) + (010)	9	35.5	-88.0	233	6.9×10 <sup>13</sup>	22
(m5p) + (000) → (m4p) + (010)	7.2	35.7	-88.0	233	8.8×10 <sup>13</sup>	22
(m6p) + (000) → (m5p) + (010)	6	35.9	-88.0	233	1.1×10 <sup>13</sup>	22
(m3p) + (010) → (m2p) + (020)	6	35.9	-88.0	233	1.1×10 <sup>13</sup>	22
(m4p) + (010) → (m3p) + (020)	4.5	36.2	-88.0	233	1.4×10 <sup>13</sup>	22
(m5p) + (010) → (m4p) + (020)	3.6	36.4	-88.0	233	1.8×10 <sup>13</sup>	22
(m6p) + (010) → (m5p) + (020)	3	36.6	-88.0	233	2.2×10 <sup>13</sup>	22
(m4p) + (020) → (m3p) + (030)	3	36.6	-88.0	233	2.2×10 <sup>13</sup>	22
(m5p) + (020) → (m4p) + (030)	2.4	36.8	-88.0	233	2.6×10 <sup>13</sup>	22
(m6p) + (020) → (m5p) + (030)	2	37.0	-88.0	233	3.2×10 <sup>13</sup>	22

TABLE IVb.  
RESONANT INTERMOLECULAR V-V ENERGY EXCHANGE RATES BETWEEN  
SYMMETRIC STRETCHING MODES OF CO<sub>2</sub> MOLECULES

REACTION	Z <sub>0</sub> /S	A	B	C	k(1500°K)	SOURCE
(lnp) + (000) → (0np) + (100)	9	34.2	-88.0	233	1.9×10 <sup>13</sup>	22
(lnp) + (010) → (0np) + (110)	9	34.2	-88.0	233	1.9×10 <sup>13</sup>	22
(lnp) + (020) → (0np) + (120)	9	34.2	-88.0	233	1.9×10 <sup>13</sup>	22
(lnp) + (100) → (0np) + (200)	4.5	34.5	-88.0	233	3.8×10 <sup>13</sup>	22
(lnp) + (030) → (0np) + (130)	9	34.2	-88.0	233	1.9×10 <sup>13</sup>	22
(lnp) + (110) → (0np) + (210)	4.5	34.9	-88.0	233	3.8×10 <sup>13</sup>	22
(mnl) + (000) → (mn0) + (001)	9	32.5	-88.0	233	3.5×10 <sup>11</sup>	22
(mnl) + (010) → (mn0) + (011)	9	32.5	-88.0	233	3.5×10 <sup>11</sup>	22
(mnl) + (020) → (mn0) + (021)	9	32.5	-88.0	233	3.5×10 <sup>11</sup>	22
(mnl) + (100) → (mn0) + (101)	9	32.5	-88.0	233	3.5×10 <sup>11</sup>	22
(mnl) + (030) → (mn0) + (031)	9	32.5	-88.0	233	3.5×10 <sup>11</sup>	22

TABLE V  
EINSTEIN COEFFICIENTS FOR SPONTANEOUS  
EMISSION

REACTION	A(sec <sup>-1</sup> )	LIFETIME(ms)	Wavelength (microns)	$\omega$ (cm <sup>-1</sup> )	Source
CO <sub>2</sub> (01 <sup>1</sup> 0) → CO <sub>2</sub> (00 <sup>0</sup> 0)	2.98	335	14.98	667.4	44
CO <sub>2</sub> (00 <sup>0</sup> 1) → CO <sub>2</sub> (00 <sup>0</sup> 0)	424.6	2.4	4.20	2349.2	45
CO <sub>2</sub> (02 <sup>2</sup> 1) → CO <sub>2</sub> (00 <sup>0</sup> 0)	11.4	88	2.75	3634.6	49
CO <sub>2</sub> (10 <sup>0</sup> 1) → CO <sub>2</sub> (00 <sup>0</sup> 0)	17.9	56	2.68	3737.4	49
CO <sub>2</sub> (03 <sup>1</sup> 0) → CO <sub>2</sub> (00 <sup>0</sup> 0)	.0022	460829	5.17	1932.5	47
CO <sub>2</sub> (11 <sup>1</sup> 0) → CO <sub>2</sub> (00 <sup>0</sup> 0)	.0166	60147	4.81	2076.9	47
CO(2) → CO(0)	0.9	1098	2.35	4260	46,48
CO(1) → CO(0)	33.4	29.9	4.67	2143	46,48
CO(2) → CO(1)	62.0	16.1	4.73	2116	46,48
H <sub>2</sub> O(010) → H <sub>2</sub> O(000)	22.1	45.2	6.27	1595.0	46,50
H <sub>2</sub> O(001) → H <sub>2</sub> O(000)	74.7	13.4	2.66	3755.8	51
H <sub>2</sub> O(100) → H <sub>2</sub> O(000)	4.0	250	2.74	3651.2	52
OH(1) → OH(0)	3.3	300	2.71	3682	20

## 9. FIGURES

1. Review of experimentally derived rate constants for the deactivation of  $\text{CO}_2$  ( $01^1 0$ ) by various collision partners.
2. Review of experimentally derived rate constants for the deactivation of  $\text{CO}_2$  ( $00^0 1$ ) by various collision partners.
3. Review of deactivation rates derived from theory<sup>22</sup> and experiment for the process  $\text{CO}_2$  ( $00^0 1$ ) +  $\text{CO}_2 \rightarrow \text{CO}_2$  ( $mn^l p$ ) +  $\text{CO}_2$ .
4. Review of experimentally derived rate constants for the V-V energy transfers between  $\text{CO}_2$  ( $00^0 1$ ) and  $\text{N}_2$  (0) or CO (0).
5. Review of experimental data for the self deactivation of  $\text{H}_2\text{O}$  ( $010$ ).
6. Review of experimental results for the deactivation of  $\text{N}_2$  (1) by various collision partners.
7. Review of experimental results for the deactivation of  $\text{O}_2$  (1) by  $\text{O}_2$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$ .
8. Review of experimental results for the deactivation of CO (1) by various collision partners.
9. Review of experimental results for the V-V transfers of energy between some diatomic molecules.
10. Review of experimental results for the deactivation of  $\text{H}_2$  (1) by  $\text{H}_2$ .

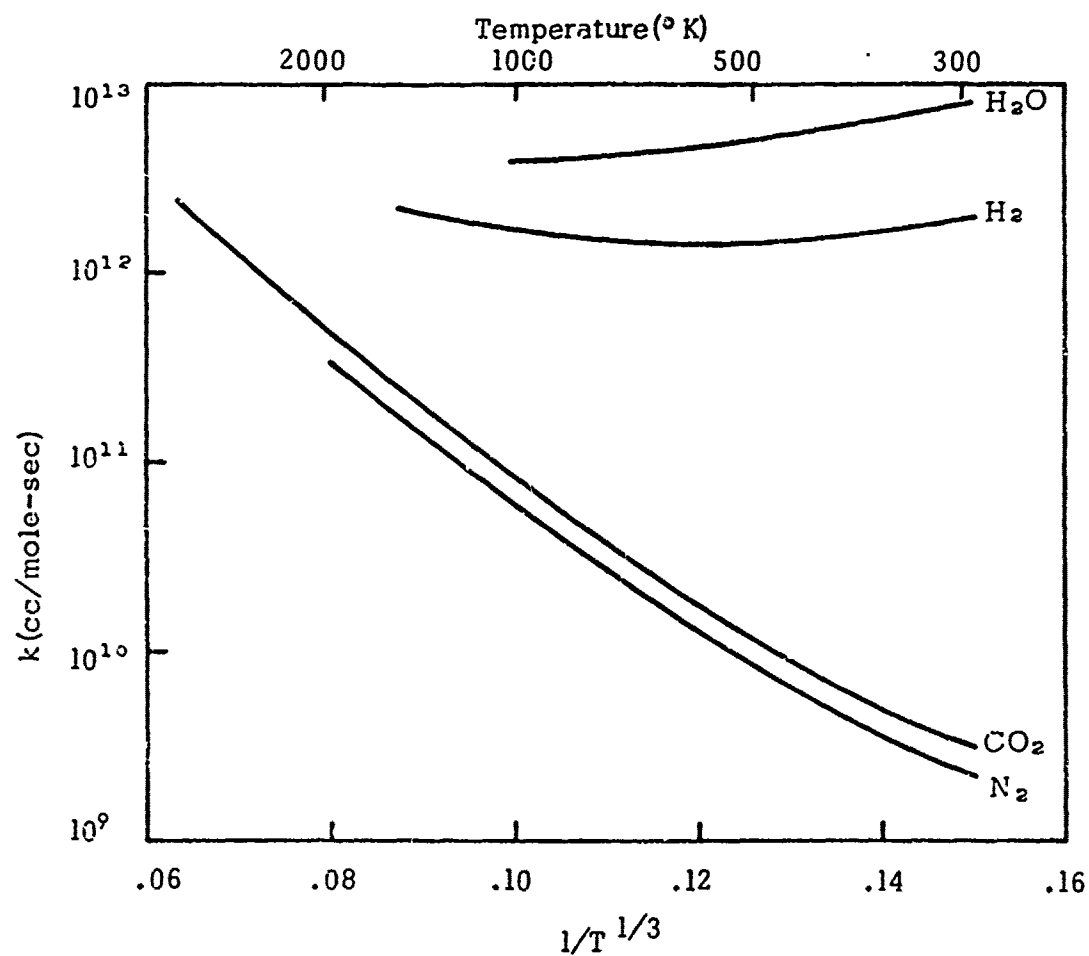
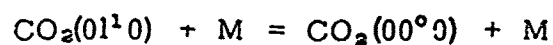


Figure 1 Review of experimentally derived rate constants for the deactivation of  $CO_2(01^1 0)$  by various collision partners



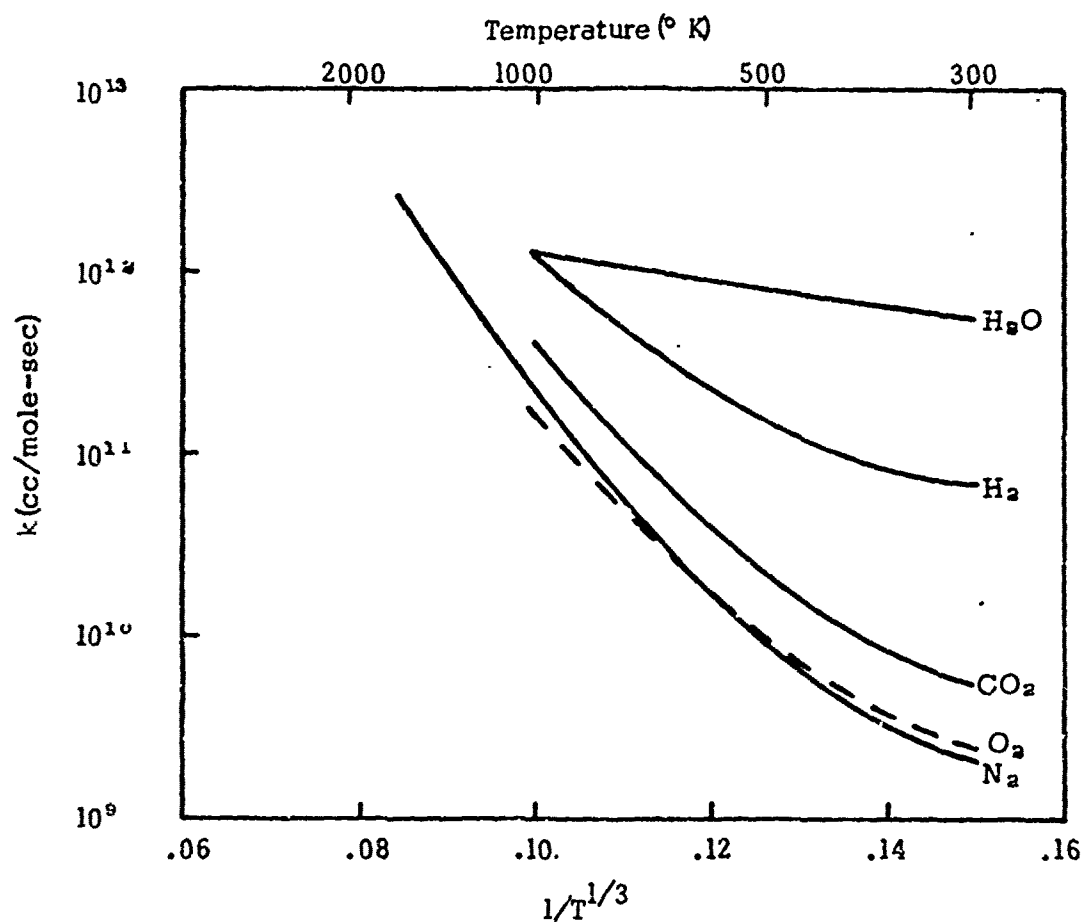


Figure 2 Review of experimentally derived rate constants for the deactivation of  $CO_2(00^u1)$  by various collision partners.



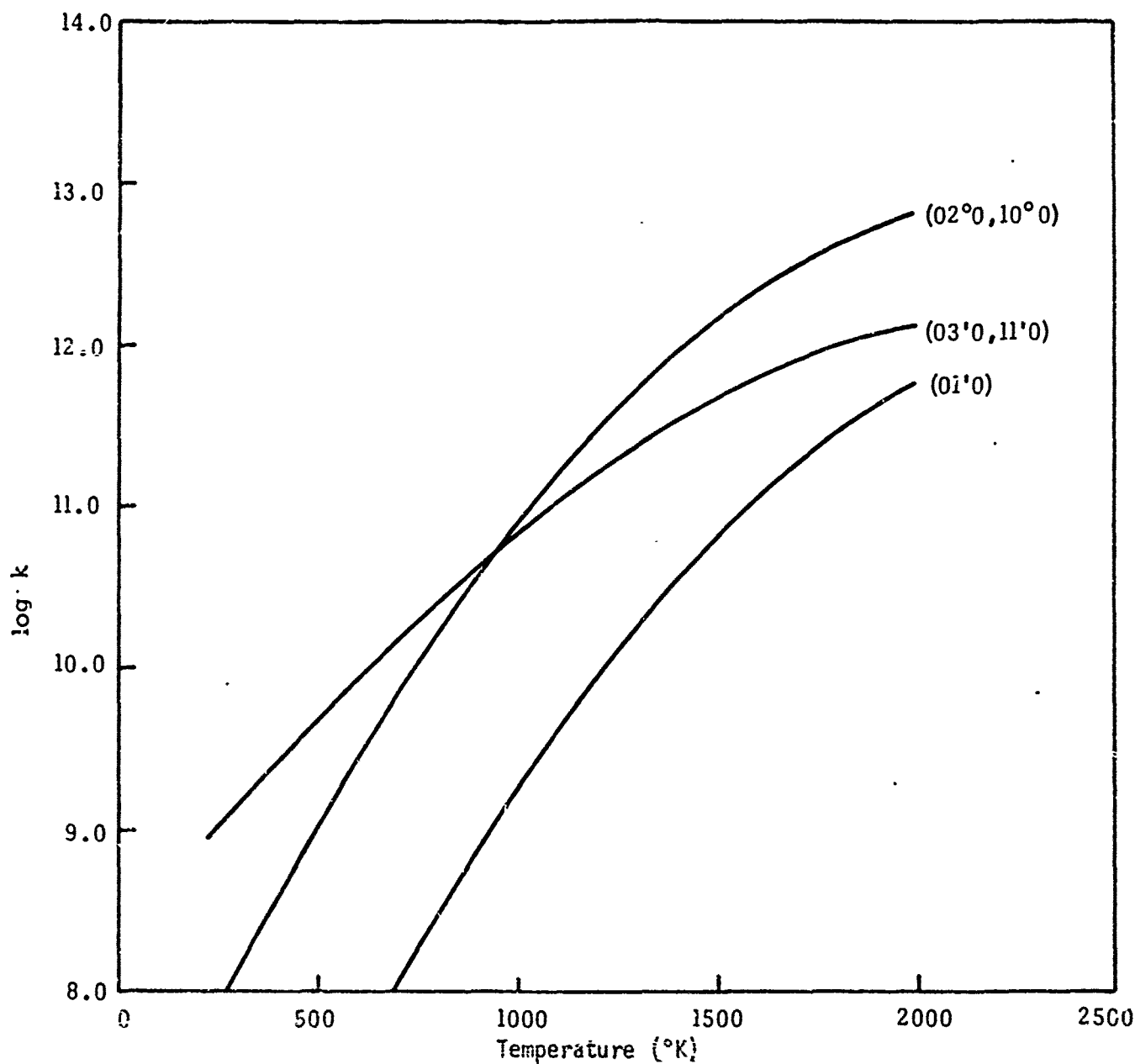
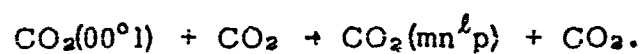


Figure 3 Review of deactivation rates derived from theory<sup>22</sup> and experiment for the process



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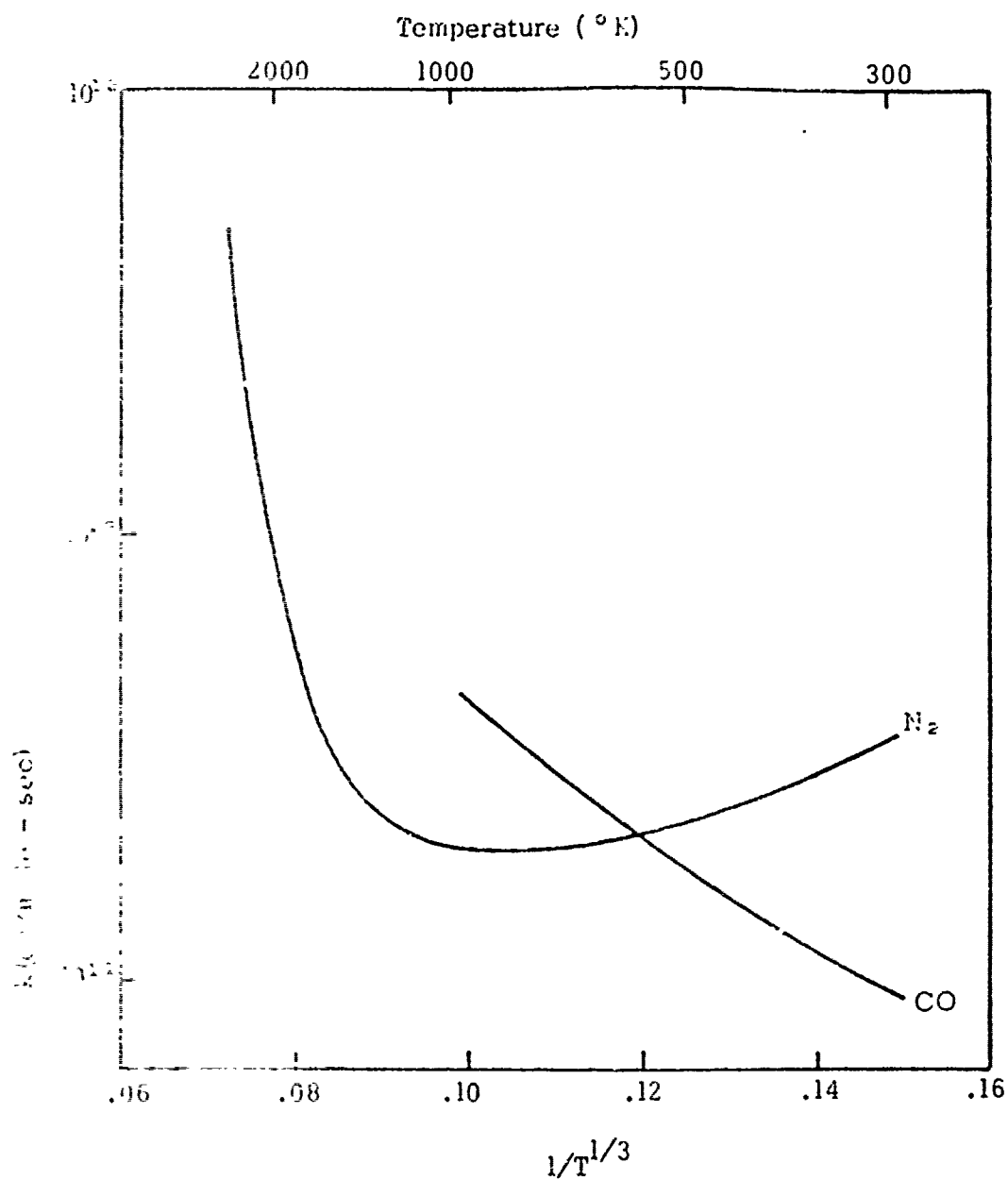
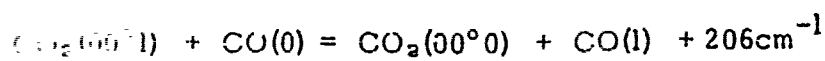
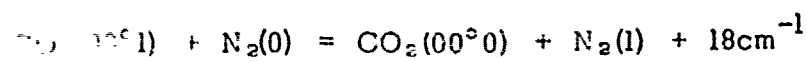


Figure 1. Review of experimentally derived rate constants for the  
energy transfers between  $\text{CO}_2(00^01)$  and  $\text{N}_2(0)$  or  $\text{CO}(0)$





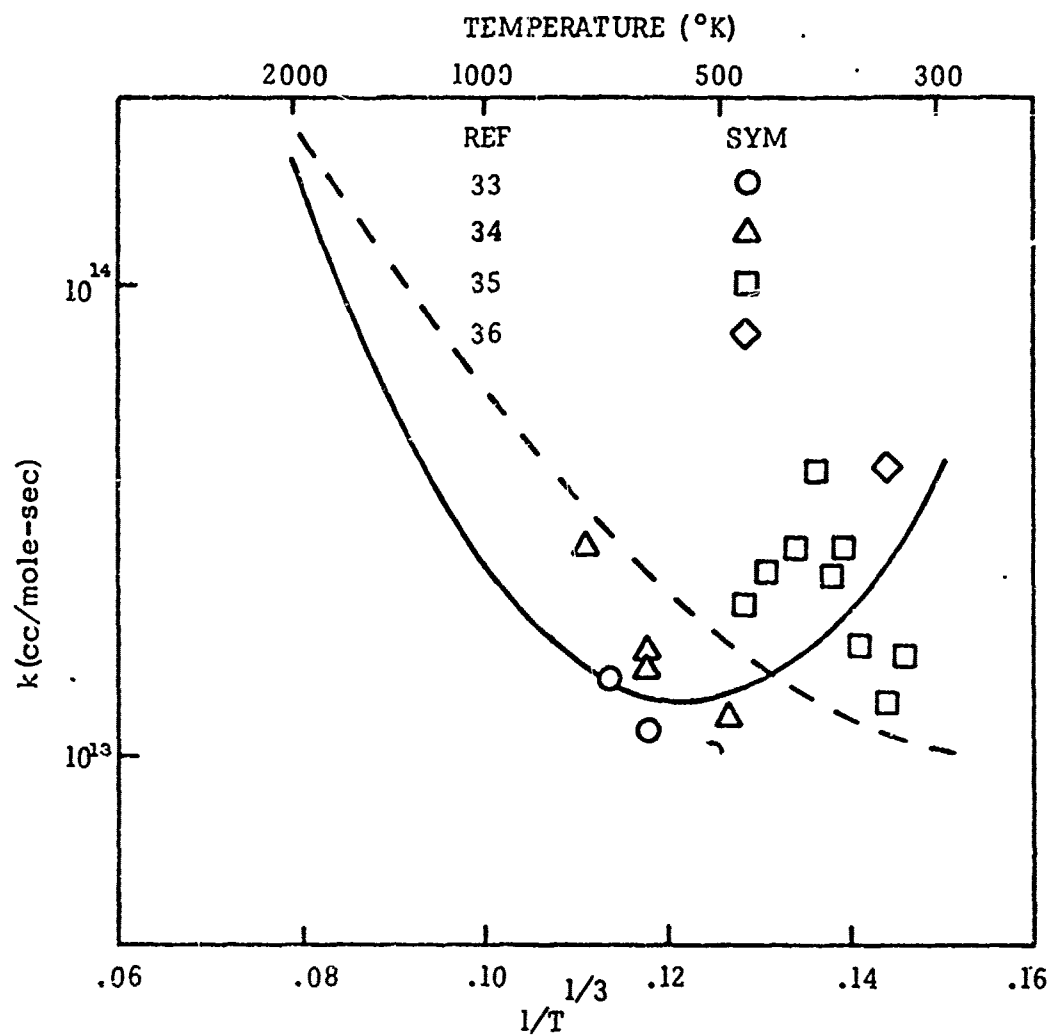


Figure 5 Review of experimental data for the self deactivation of  $H_2O(010)$ .



Shin V-T exchange (37) ——— ; Shin V-R exchange (70) - - - - -.

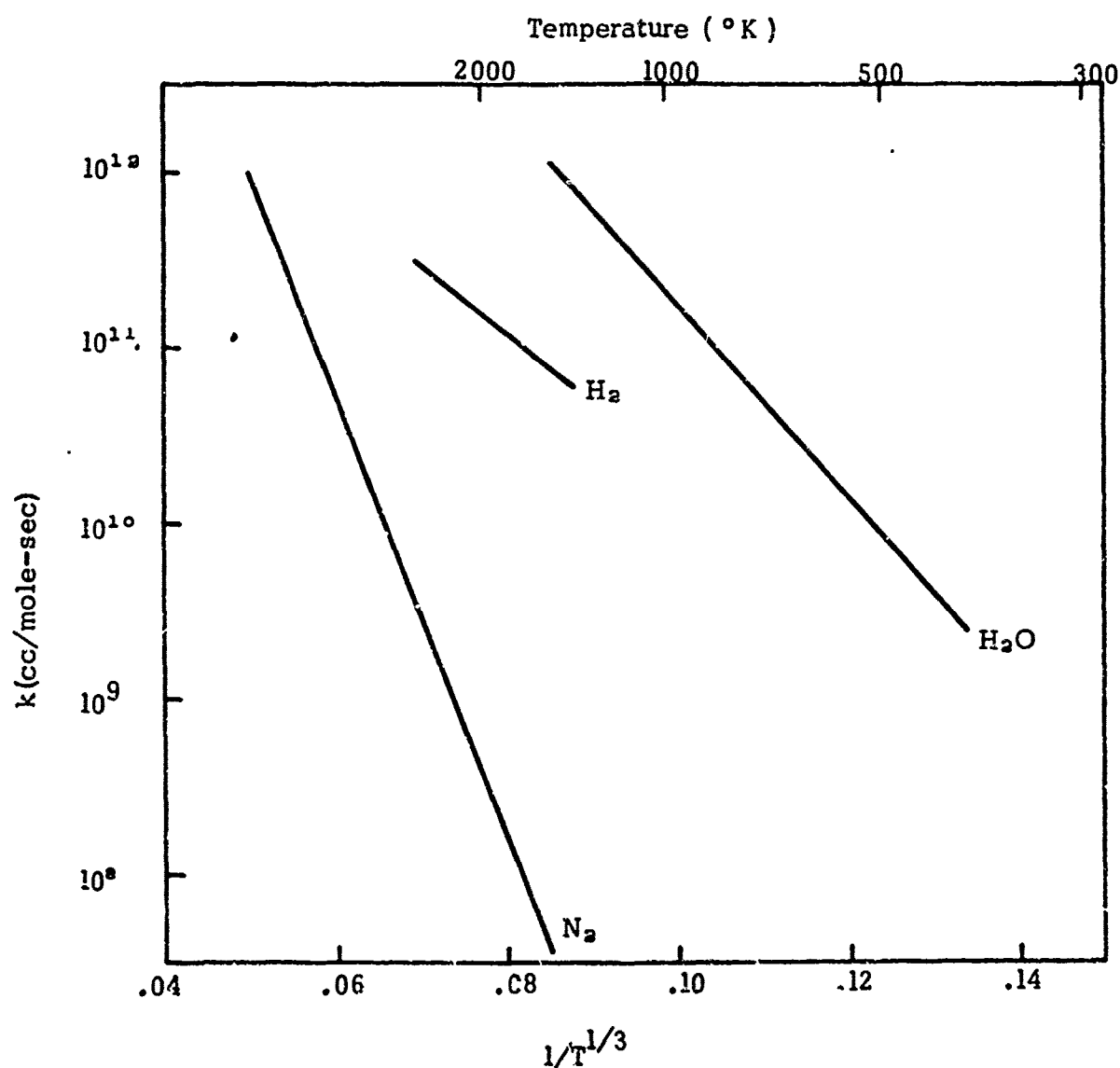


Figure 6 Review of experimental results for the deactivation of  $\text{N}_2(l)$  by various collision partners



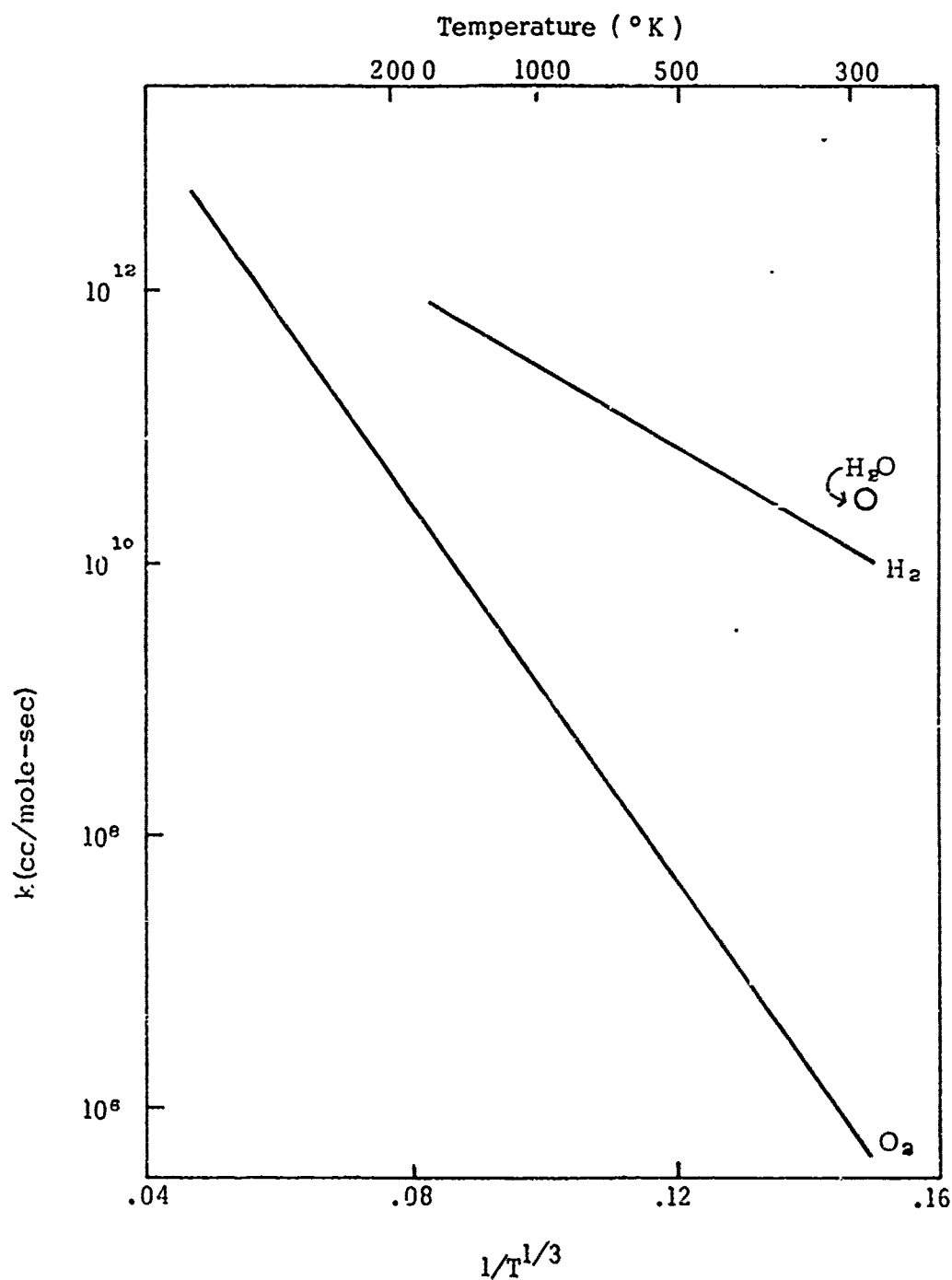


Figure 7 Review of experimental results for the deactivation of  $\text{O}_2(l)$  by  $\text{O}_2$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$ .



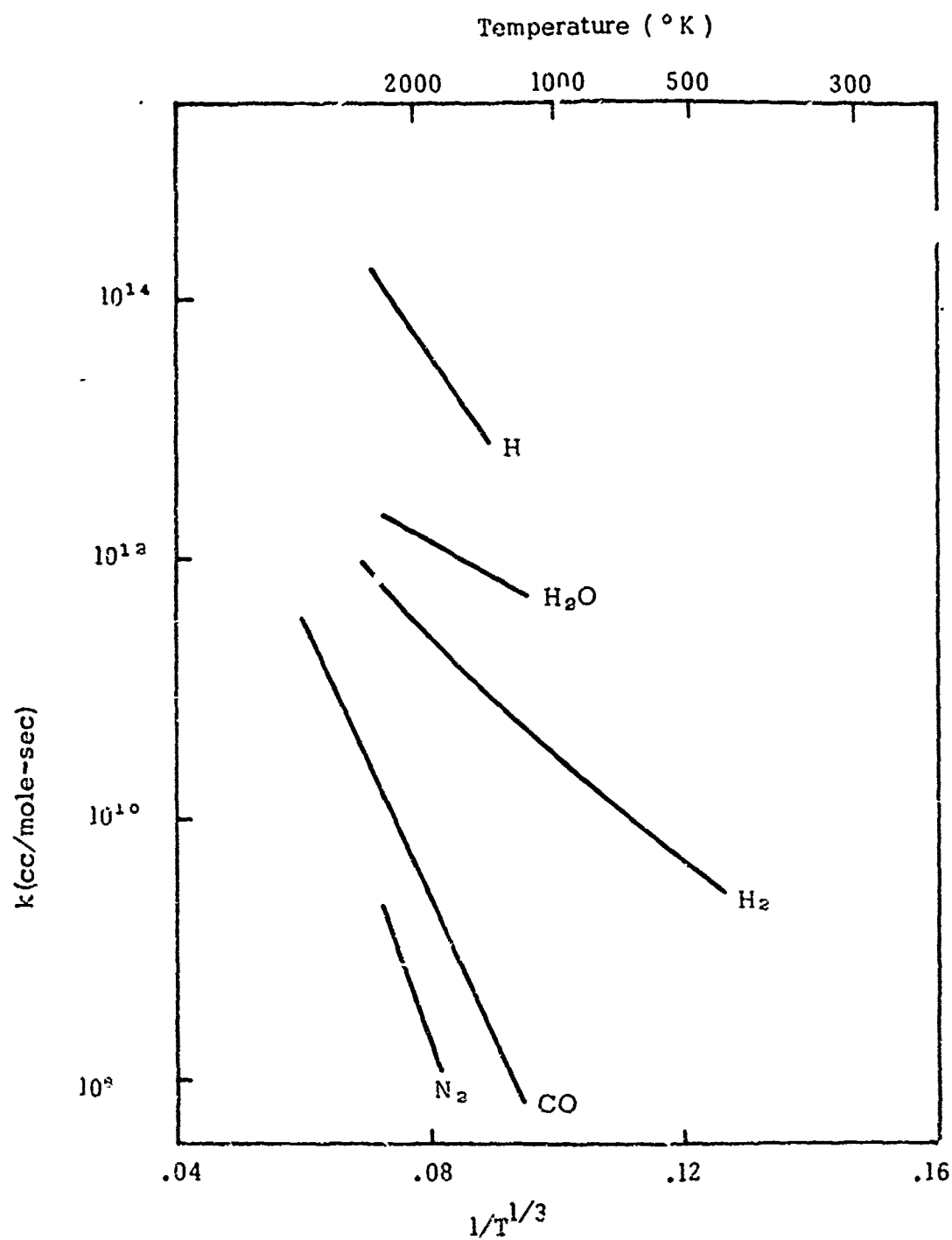


Figure 8 Review of experimental results for the deactivation of  $\text{CO(l)}$  by various collision partners  $\text{CO(l)} + \text{M} \rightarrow \text{CO(0)} + \text{M}$ .

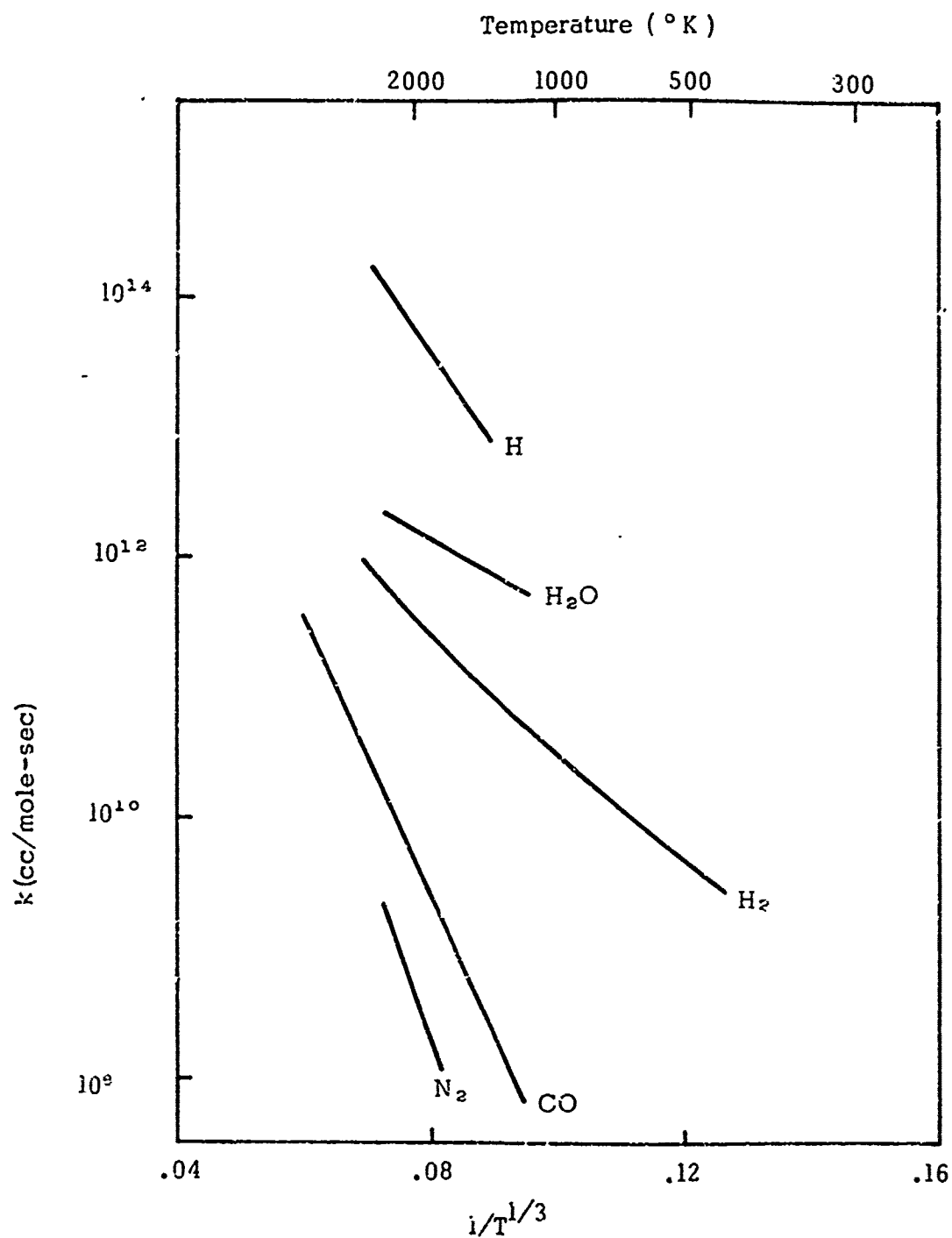


Figure 5 Review of experimental results for the deactivation of  $CO(l)$  by various collision partners  $CO(l) + M \rightarrow CO(0) + M$ .

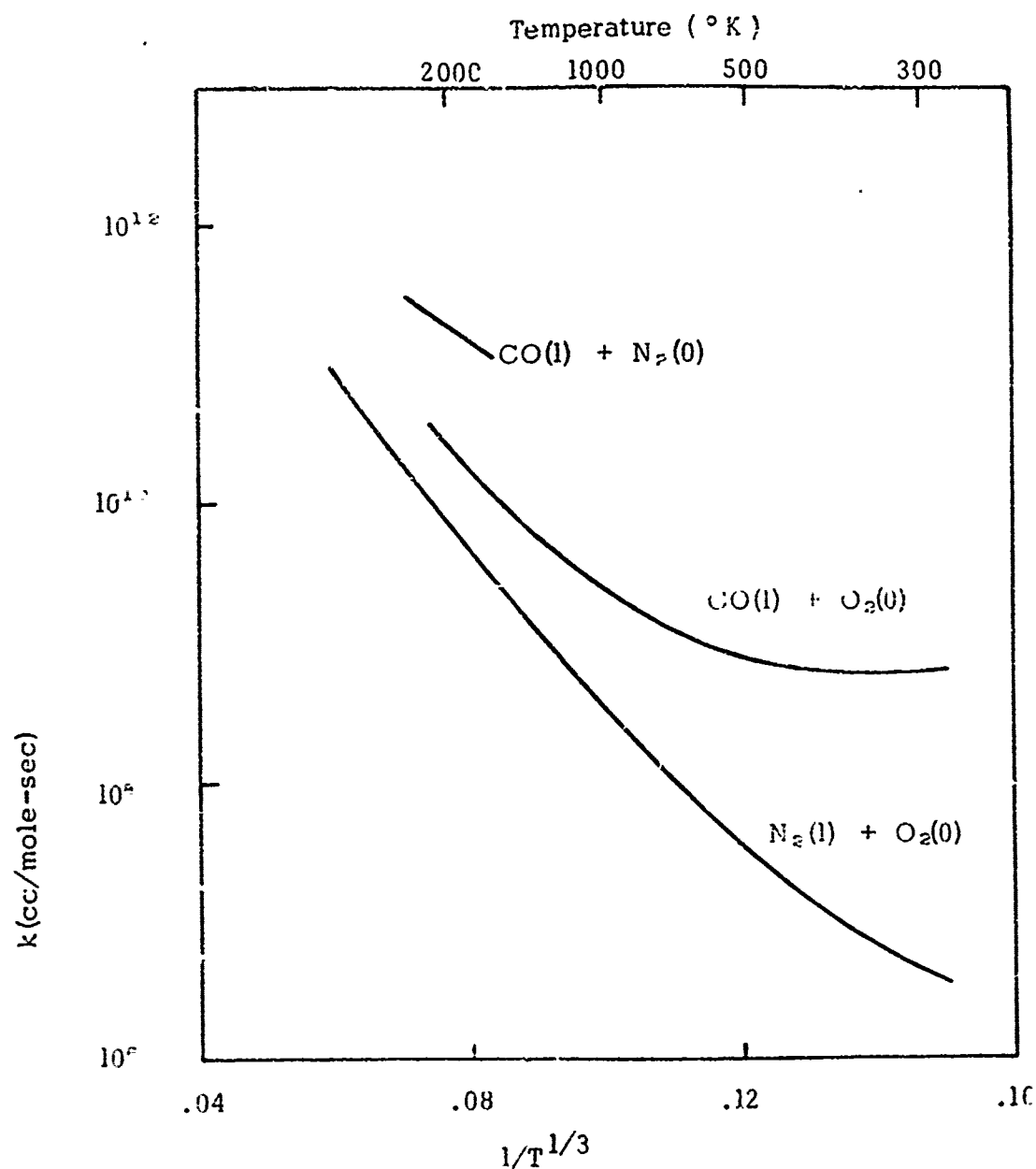
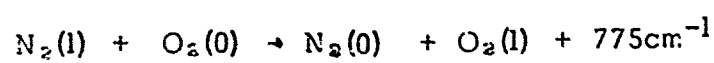
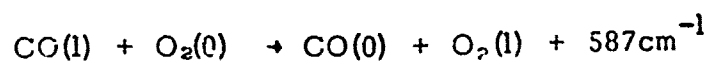
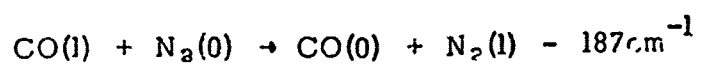


Figure 9 Review of experimental results for the V-V transfers of energy between some diatomic molecules.



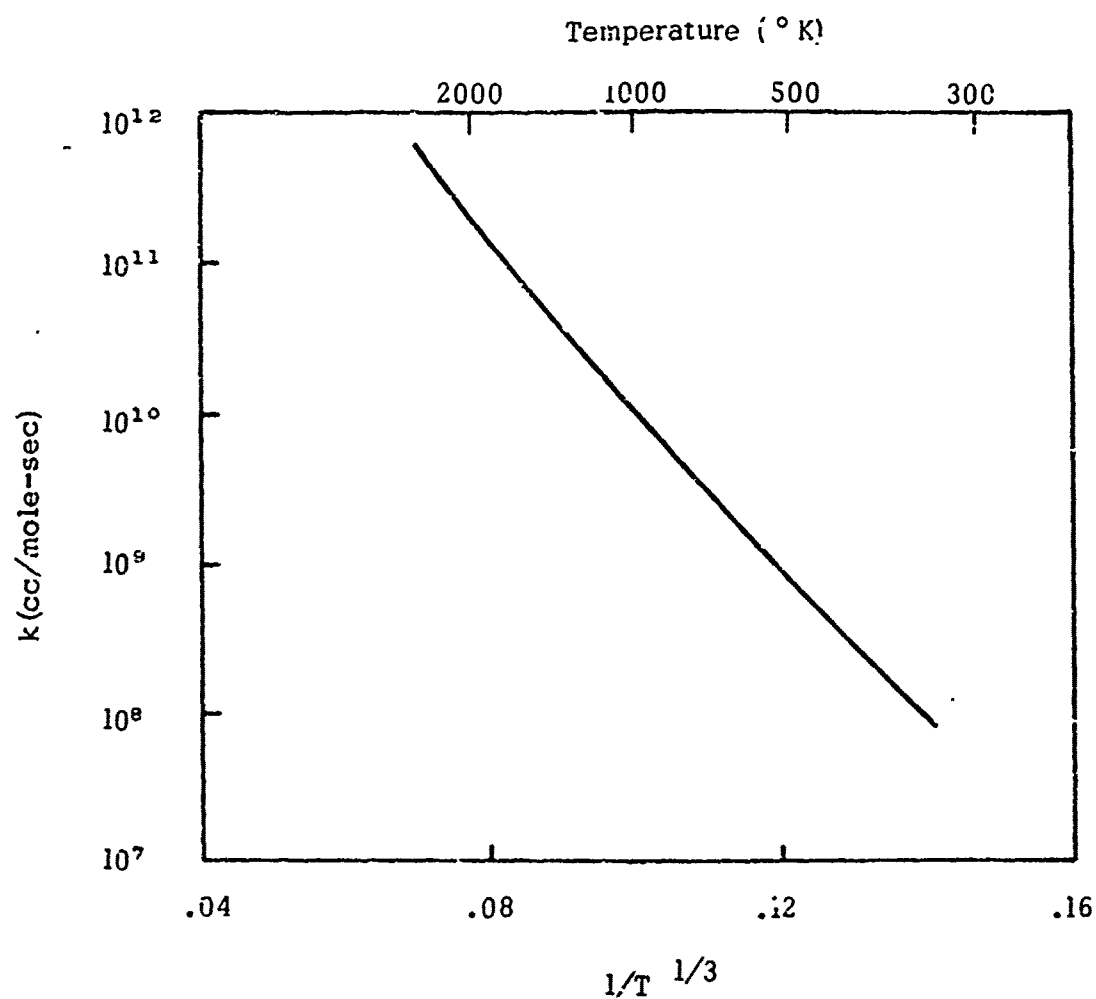


Figure 10 Review of experimental results for the deactivation of  $H_2(l)$  by  $H_2$



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